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Oxidation Kinetics of K Basin Fuel (OCRWM)

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EXECUTIVE SUMMARY

Oxidation testing of K Basin-stored N Reactor fuel in dry air, moist air, and moist helium provided reaction rate data for the Spent Nuclear Fuel Project. The tests were performed on small samples from two spent nuclear fuel elements retrieved from the closed canisters of the K West Basin. The spent nuclear fuel samples were tested using a thermogravimetric analysis system modified for moist-gas operation to allow testing in moist environments. The tests were run at constant temperature and water vapor pressure.

The moist helium tests used 6.5 kPa water vapor, producing seventeen data between 75°C and 210°C. Eight of these data were excluded from primary consideration due to testing anomalies and balance drift issues. Regression analysis of the nine acceptable data provided good assurance that the moist-helium results are consistent with literature data within the temperature range of 25°C to 210°C. Concerns about possible oxygen poisoning from air in-leakage and mass transfer limitations on the test data were reviewed. If oxygen poisoning occurred it was not likely to have biased the data sufficiently to change the basic conclusions of comparability to the literature data. Mass transfer limitations did not appear to have had significant effect on the moist-helium data.

Seventeen tests in dry air provided seven acceptable data from 70°C to 275°C. Results from the remaining ten tests were not used due to erratic weight gain data and other test anomalies. Four of the good data were in agreement with the literature data from 200°C to 275°C. The data at low temperature (below 150°C) could not be compared to the literature data due to uncertainty that the measurements provided linear reaction rate values.

Four spent nuclear fuel data from tests in moist air with 12 kPa water vapor at 200°C and 350°C agree with the literature rate within the temperature range tested. These data could not be adequately extrapolated to provide comparability to the literature rate at low temperature.

Many of the spent nuclear fuel test samples fragmented during the oxidation testing. A review of the posttest observations and test data concluded that temperature was a probable influence on sample deterioration. No breakage was observed at test temperatures below 140°C, and about one-half of the samples tested above 150°C cracked or fragmented. The degree of fragmentation seemed to increase somewhat with temperature. Another possible influence was sample integrity due to proximity to damaged surfaces on the fuel from which they were derived.

The qualification status of the data referenced and used in this document are “existing” as defined in DOE/RW-0333P (DOE 1998).

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List of Acronyms

CI	Confidence Interval
CL	Confidence Limit
CVD	Cold Vacuum Drying
DIRT	Data Integrity Review Team
DQO	Data Quality Objective
MCO	Multi-Canister Overpack
OCRWM	Office of Civilian Radioactive Waste Management
PI	Prediction Interval
PNNL	Pacific Northwest National Laboratory
QARD	Quality Assurance Requirements and Description
SNF	Spent Nuclear Fuel
TGA	Thermogravimetric Analysis

OXIDATION KINETICS OF K BASIN FUEL (OCRWM)

1.0 INTRODUCTION

The Hanford N Reactor spent nuclear fuel (SNF) is stored in water in the Hanford K East and K West Basins. The fuel material is metallic uranium clad in Zircaloy-2. Many of the fuel elements were damaged upon discharge from the reactor exposing the uranium to the water, resulting in corrosion and deterioration of the fuel. The SNF Project will load the stored fuel into multi-canister overpacks (MCOs), vacuum/inert-gas dry the fuel at about 50°C, and place them into interim storage, according to the recommendations of the Integrated Process Strategy (Gerber 1996). Exposure of the damaged fuel surfaces to heated moisture during drying and to air under accident conditions will oxidize the uranium, causing exothermic heating of the fuel elements. The modeling of these processes and accident conditions require an understanding of the reaction rate of the K Basin fuel material with moisture and oxygen. Published literature sources provide reaction rate data and rate law equations for unirradiated, pristine uranium and uranium fuel in the various environments as a function of temperature and gas pressure. Some data and understanding are available for irradiation effects on oxidation kinetics, but an understanding of the effects of surface damage and corrosion on the reaction rate of N Reactor fuel material is needed to assure that proper adjustments are made to the available rate law(s).

A Data Quality Objectives (DQO) process was used to establish the needs and requirements for measuring the reaction kinetics of K West Basin fuel in support of the SNF Project (Lawrence 1995b). A Thermogravimetric Analysis (TGA) system was selected for these measurements. Small samples of K West Basin fuel and unirradiated N Reactor fuel have been tested, providing oxidation rate measurements as a function of temperature in three environments: dry air, moist-air and moist-helium. The purpose of this report is to present the laboratory data, to discuss the data in light of experimental uncertainties, and to provide an evaluation of the data relative to the rate law equations from the current literature.

The reaction rate of K Basin SNF relates to the conditioning of these fuel into their final form for repository disposal. As such the requirements of DOE/RW-0333P (OCRWM) apply to these data (Sellers 1995). This request has been peer reviewed in accordance with those requirements.

During the development of the moist-helium test data, detailed expert reviews were performed to ensure data quality. Three types of reviews were held.

1. Characterization team reviews: Weekly reviews were held with the Pacific Northwest National Laboratory (PNNL) scientists performing the experiments as well as the SNF characterization team. The latest data was reviewed real time.
2. Data Integrity Review Team (DIRT): The team consisted of three scientists and one engineer with expertise in reaction rate data development and use. This team was assembled to review TGA experimental procedures as well as the integrity of the data. The team met on at least a weekly basis. The DIRT has concluded that the experimental procedure was adequate and the data collected are of high quality.

3. Senior Review Panel: A senior review panel was assembled to review the results of the data. This team consisted of Hans Fauske, Phil Loscoe, and Alden Segrest/Joe Swenson. The team met on four occasions and determined that the results of the TGA experiments are appropriate.

These reviews improved the confidence in the moist-helium data and helped to put a new perspective on the dry-air data.

2.0 DATA QUALITY OBJECTIVES

The DQO for reaction rate studies of K West Basin fuel identified that chemical reaction rate data were needed by the SNF Project to benchmark basic input for the following analysis models: MCO air ingress, cold vacuum drying (CVD), and passivation phase conditioning (Lawrence 1995a). The fuel passivation (hot conditioning) phase of the K Basin fuel processing has since been canceled from the SNF Project and, therefore, is not addressed by these tests. Other data needs were also identified by the DQO, which are outside the scope of this report. For example, the pyrophoric property of the fuel was identified as a need. Ignition tests were performed and documented (Abrefah et al. 1998c), but these data are outside the scope of this report. The scope of this document includes only the reaction rate of K Basins fuel at CVD and air ingress conditions.

The DQO decision boundaries for the reaction rate tests included TGA test parameters that would explore conditions reported in the literature. The measured values for the irradiated fuel would be compared to literature values.

A decision rule and acceptance limits were not provided by the DQO, as acceptance criteria were not available (Lawrence 1995a). Thus, any test results that were produced within the calibration tolerance may be considered acceptable.

The DQO stated that fuel samples selection should be made to bound the (fuel element) conditions expected to be found in the basins and that testing damaged and undamaged areas of two fuel elements would do this. Fuel had been previously selected from the K West Basin to bound the fuel conditions expected to be encountered in the closed canisters of the basin (Lawrence 1995a). The TGA measurements of these fuel elements were expected to provide data to bracket expected conditions, and the data would be compared to data from previously published sources, i.e., the literature data. These initial tests were to provide the basis for more extensive testing using samples from follow-on fuel sampling campaigns (Lawrence 1995a).

Subsequent DQO documents were issued providing requirements for TGA testing of fuel from the K East Basin and from a second fuel sampling campaign in the K West Basin (Lawrence 1996; Lawrence et al. 1997). These tests were to include reaction rate measurements. The data would be used to evaluate differences that may exist for fuel stored in the open canisters of the K East Basin as compared to that in the closed canisters of the K West Basin. The tests would also examine the extent and diversity of fuel damage as indicated by the in-basin examinations.

Due to updated SNF Project needs and schedules, it was determined that only one K West Basin fuel element would be TGA tested in moist-helium (Sellers 1998). Whole element testing of K East and K West fuel elements was completed, which provided limited data regarding reaction rates (Lawrence 1999). The whole element test data are not addressed in this report.

Validation of the subject data to these DQO requirements are discussed in Section 5.5.

3.0 REACTION RATE MEASUREMENTS AND DATA

The dry-air, moist-air, and moist-helium tests and results were documented by Abrefah et al. (1998a, 1998b, 1999). Literature reviews of oxidation rate data for dry air and oxygen-free moisture have been documented (Trimble 1998a, 1998b).

The reaction kinetics data for K Basin SNF were derived from weight-gain measurements using small samples obtained from two damaged K West Basin fuel elements.

The weight-gain measurements were made using a TGA system having capabilities in accordance with the DQO requirements (Lawrence 1995a). The calibration of the TGA system was maintained within the requirements of the DQO as appropriate to these tests. Calibrations included balance accuracy ($\pm 0.1\%$) and temperature measurements ($\pm 1^\circ\text{C}$). While temperature measurement accuracy was within the DQO allowable ($\pm 1^\circ\text{C}$), actual sample temperature may have been, in some cases, as much as 10°C above the measured value (Cramer and Abrefah 1997). This was due to potential self-heating of the sample and distance of the thermocouple from the sample. Based on data error analysis this uncertainty on temperature has been determined to be acceptable (Appendix A). The only procedural requirement specified by the DQO for reaction rate testing related to preconditioning of some samples. This was not done because of changes in the fuel processing requirements that had evolved within the SNF Project, i.e., hot condition had been removed. The data generated from the TGA measurements are within acceptable calibration tolerances and are of acceptable quality for its intended use, except as noted in Section 5.5.

Measurements in Air

Seventeen measurements were made in dry air using samples from the damage region of two fuel elements. Many of these measurements were unusable due primarily to erratic weight gain data while seven tests provided good rate data (Abrefah et al. 1998a). The erratic data were due to losses of oxidation products from the sample cup and equipment problems during the tests. Two dry-air measurements were also obtained from the undamaged region of one element, and two tests were performed using unirradiated N Reactor fuel material. The temperature of the dry-air data range from 69°C to 275°C . Figure 1 compares dry-air data for damaged and undamaged SNF and unirradiated fuel data to the literature review data. The prediction interval (PI) on the literature data is shown in Figure 1 to indicate the interval over which there is 95% confidence that the next added datum might lie.

Five moist-air tests were performed using samples from the damaged end of one fuel element. Three of these tests provided reaction rate data (Abrefah et al 1998b). Figure 2 shows moist-air and dry-air data for SNF relative to rate law equations for unirradiated uranium (Trimble 1998a; Pearce 1989).

Note that the SNF data for dry-air and moist-air tests (Figure 2) show no difference in oxidation rate within the overlapping temperature region. However, the rate laws for oxidation of unirradiated uranium indicate an order of magnitude difference for these two environments. To explain this observation, Abrefah et al (1998b) provides a hypothesis that microcracks and a matrix of hydride in samples of damaged and corroded SNF may influence oxidation rate such that any enhancement effects due to moisture added to the air becomes negligible.

Measurements in Moist Helium

TGA tests were performed in moist-helium using seventeen samples from the damaged end of one K Basin fuel element and four unirradiated N Reactor fuel samples. Nine of the SNF tests and three unirradiated material tests provided useful moist-helium reaction rate data (Abrefah and Sells 1999). The remaining tests had issues relating to measurement accuracy.

The moist-helium TGA data are plotted in Figure 3, comparing them with the literature data for uranium in oxygen-free water vapor and the equation for unirradiated uranium in water vapor from Pearce (1989).

Qualification Status

The data referenced above were not acquired or developed in accordance with an approved quality assurance program in accordance with the Office of Civilian Radioactive Waste Management (OCRWM)/Quality Assurance Requirements and Description (QARD) (DOE 1998), and they have not been qualified in accordance with OCRWM/QARD. As such, the qualification status of the data are "existing" as defined in OCRWM/QARD.

Figure 1. Oxidation of Uranium and K Basin Fuel in Dry Air

Figure 2. Oxidation of Uranium and K Basin Fuel in Dry and Moist Air

Figure 3. Oxidation of Uranium and K Basin Fuel in Moist-Inert Gas

4.0 ERRORS AND UNCERTAINTIES

Measurement errors and test environment uncertainties can influence data reliability. Errors in the rate constant values include uncertainties in measuring weight gain, surface area, temperature, test time, and water vapor pressure. Test environment uncertainties include oxygen content in the helium test atmosphere, mass transfer limitations and sample fragmentation effects. When establishing a rate law from experimental weight gain data, one must ensure that the observations being compared correspond to the same extent of reaction or reaction progress.

A statistical analysis of the moist-helium data is included in the data report for those tests (Abrefah and Sells 1999). Additional error analyses for the dry-air data and the moist-helium data are included in Appendix A. Oxygen poisoning effects are examined in Appendix B, and sample fragmentation observations and analyses are provided in Appendices C and D.

4.1 MEASUREMENT UNCERTAINTIES

Reaction rate measurement errors and uncertainties are evaluated for the dry-air and moist-helium data in Appendix A. Propagation of error analysis was based on the measured and assumed uncertainties on the measurement of weight gain, surface area, time, temperature, and water vapor pressure. Total test times of the dry-air tests were also evaluated in Appendix A for sufficiency based on reaction progress considerations.

Moist-Helium Data

Results of the moist-helium data error analysis in Appendix A (Figure A.5) indicate a large uncertainty on the K Basin fuel data below about 110°C and low to moderate uncertainty above 150°C. These uncertainties notwithstanding, the measured data are seen to lie below or within the literature data and do not exceed the upper 95% prediction interval for the literature data.

Replicate measurements were made at several temperatures with good reproducibility of the measurements. The statistical analysis in Abrefah and Sell (1999) evaluates the pure error for the moist-helium data based on replicate tests. A relative error of about 31% at one standard deviation was found. This is a measure of the variability of the data due to sample and test variabilities.

The overall conclusion of the statistical analysis in Abrefah and Sell (1999) was that no evidence was found that the K West SNF data were higher than literature data.

Dry-Air Data

Error analysis of the dry-air data was not done due to insufficient understanding of the measurement errors (Appendix A). In addition an analysis of the reaction progress for the low temperature (below 150°C) tests indicated a significant uncertainty that those data represent linear kinetics for the material tested. The initial stages of dry-air oxidation are nonlinear, and the test time at low temperature may not have been adequate to reach the linear stage of the reaction. The possible effect of this would be to measure a reaction rate that is higher than the

linear rate, and therefore would not be a valid comparison to the linear rates of the literature data. (It is assumed that the literature data represents sufficiently long tests to measure the linear rates.) Since replicate tests were not performed for SNF in dry air, the variability in the measurements could not be determined.

For these reasons (no error analysis, reaction progress uncertainty, and lack of replicate data) the low temperature, dry-air reaction rate data cannot be evaluated for comparability to the literature data.

The uncertainties for the high temperature data (greater than 150°C) are likely to be smaller than for the low temperature data, but are unknown. These data fall within the spread of the literature data, but without replicate data or an error analysis they cannot, without some reservation, be validated as equal to the literature data.

4.2 OXYGEN CONTAMINATION

The moist-helium test atmosphere may have been contaminated with oxygen, which at levels exceeding about 10 ppm would depress (poison) the reaction rate compared to oxygen-free moisture (Abrefah and Sell 1999). The suspected contamination was based on a measurement of 80 ppm oxygen at a point downstream from the sample reaction chamber. Abrefah and Sell concluded that the oxygen was probably the result of in-leakage downstream of the test chamber, since measurements found less than 10 ppm in the helium supply and precautions had been used to assure that contamination would not occur as the gas entered the system. An evaluation of the feasibility that downstream in-leakage might contaminate the test environment was performed by Epstein of FAI (Appendix E). This analysis determined that the assumed downstream in-leakage would not result in significant oxygen at the sample reaction chamber.

In the event that oxygen contamination did occur in the sample reaction chamber, the possible effect on the reaction rate is evaluated in Appendix B. This analysis indicates that oxygen levels above about 25 ppm in a moist inert gas will reduce the reaction rate of uranium, and levels of more than about 150 ppm reduce rates by a factor of seven to eight. Oxygen at 80 ppm would have a somewhat lesser effect than 150 ppm. Assuming the maximum effect of oxygen, the analysis in Appendix B indicates that most SNF data, when adjusted for the oxygen poisoning effect, are below the upper bound of the 95% prediction interval for the literature data for oxygen-free water vapor.

4.3 MASS TRANSFER LIMITATIONS

Gas flow rate was reduced from the initial test runs to reduce mass loss from the sample cup. Should the potential reaction rate of the uranium exceed the rate of supply of the reactant at the reduced flow, the measured rate will be biased low. Such mass transfer limitations would occur most readily at the highest test temperatures, since the reaction rate is greatest there. Within the range of temperature in which a given reactant supply rate would limit the reaction rate, the rate would not change with temperature. In addition increased flow at a given temperature should result in increased reaction rate when the flow increase becomes sufficient to overcome a reactant supply limitation.

The SNF moist-helium data do not support a mass transfer limitation problem for these reasons: An inspection of the data in Figure 4 shows that reaction rate does not increase with flow rate, and reaction rate does increase with temperature to at least 160°C.

4.4 SAMPLE FRAGMENTATION

If a sample were to fragment during a reaction rate measurement, the increased surface area may cause the rate per initial surface area to increase. Three moist-helium test specimens were found broken in posttest examinations. These tests were at approximately 160°C and produced rate data somewhat higher than other 160°C data (Figure 3). A quantification of the fragmentation effect was not feasible because the surface area of the fragments could not be readily assessed. Additionally, the point-in-time of the fragmentation was unknown, as was the rate of fragmentation.

Figure 4. K Basin Fuel Reaction Rate Data with Test Atmosphere Flow Rates

5.0

DISCUSSION

5.1 OXIDATION IN MOIST HELIUM

Figure 5 compares the 95% confidence interval (CI) on the mean of the SNF data to the mean of the literature data. The statistical upper limits on the mean of the SNF data do not exceed those of the literature data between 25°C and 210°C. Although possible oxygen contamination of the TGA test atmosphere may have occurred, conservative adjustments to the measured rate constants to account for this possibility indicate that the SNF rates in the absence of oxygen would not, in general, exceed that predicted from the literature data (Appendix B). Figure 3 shows the good comparability of the mean of the literature data to the rate law equation from Pearce (1989). Thus, the mean reaction rate of the SNF results in moist-helium, including an extrapolation to 25°C, do not exceed that predicted by the following rate law equation from Pearce (1989):

$$\text{Log } k = 4.33 - 2144/T + 0.5 \text{ Log } (P) \quad (5.1)$$

5.2 OXIDATION IN DRY AIR

A linear fit to the low temperature SNF test data in dry-air indicates rates higher than the literature values. However, it has been determined that the SNF rates cannot be adequately compared to the literature data (Appendix A). Error analysis on the dry-air data was not possible, and the low temperature tests may not have been run long enough to have measured linear kinetics for the K Basin SNF. The literature-data rate law for dry-air oxidation could not be confirmed as applicable to the K Basin fuel, nor could it be refuted.

5.3 OXIDATION IN MOIST AIR

The moist-air values for SNF in 12.3 kPa water vapor are comparable though somewhat below that predicted by the following literature rate (Pearce 1989) for unirradiated uranium in moist-air (Figure 2):

$$\text{Log } k = 6.193 - 2963/T + 0.3 \text{ Log } (P) \quad (5.2)$$

Due to the limited temperature range and number of SNF data, the data cannot be extrapolated with sufficient accuracy to determine how the low temperature reaction rate of K Basin fuel compares to the literature rate at low temperature (below 150°C).

5.4 SAMPLE FRAGMENTATION

Some samples fragmented during oxidation testing. The fragmentation occurred to varying degrees, from cracking to fracture to disintegration. A review of sample fragmentation (Appendices C and D) indicates that the phenomenon is influenced by temperature. Fragmentation begins at about 140°C, with about 50% of the samples fragmenting when tested above 140°C in dry air, moist air or moist helium.

Figure 5. Comparison of the Reaction Rate Data for Moist-Inert Gas Oxidation for a K West Basin Fuel and from the Literature

Sample fragmentation can increase the test surface area and thus, has the potential for biasing reaction-rate data high. Three tests in moist helium disintegrated during testing at about 160°C. The reaction rate data for these tests were somewhat higher than the remaining moist helium data at 160°C, indicating a possible, moderate effect of increased surface area (Figure 3).

Sample disintegration in some of the dry and moist air tests created problems for these data. When fine, dispersible powders were created by the oxidation, these particles were at times lost from the sample cup causing weight loss and erratic data. The erratic data made the tests unreliable and were not used in the oxidation kinetics evaluations. Of the seven of the dry air tests that provided data for kinetics evaluations, two had fragmented samples. These tests, at 225°C and 275°C, did not show rates higher than for the literature data or for the other dry air SNF tests in that temperature range.

5.5 DATA VALIDATION

DQO requirements (Lawrence 1995a) for chemical reaction rate data for K West Basin fuel in vacuum drying conditions have been partially satisfied. Samples from the damaged and undamaged areas of two fuel elements were TGA tested providing reaction rate data in dry-air, and the damaged areas of one fuel element were tested in moist-air and moist-helium conditions. The dry- and moist-air data relate to air-ingress accident conditions, and the moist-air and moist-helium data relate to CVD of the fuel.

The moist-helium tests provided adequate numbers of data and quality of data over a sufficient range of temperatures to benchmark the input for the air ingress and vacuum drying analyses and the data are qualified "Use As Is" as defined in Lawrence (1998). These data have been reviewed and compared to the appropriate literature data and rate laws.

The numbers of moist-air tests were limited and evaluated a limited temperature range. While the results were in agreement with the appropriate rate law equation at the temperatures tested, the data could not be adequately extrapolated to conditions of interest and therefore are qualified "Limited Use" as defined in Lawrence (1998). Limited Use data are accepted for their intended use with limitations as to what conclusions they may be used. The limitations are that they may not be used to compare to literature data at low temperature (below 150°C).

The dry-air tests provided results at low temperature (below 150°C) for which the quality could not be validated and are therefore given the status "Reject" as defined in Lawrence (1998). The high temperature dry-air data are "Limited Use." They may not be used to compare to literature data at low temperature (below 150°C). Resampling or revalidation of the dry-air data will not be required because it has been determined that fuel process and safety analyses do not require the data (Pajunen 1999).

6.0 CONCLUSIONS

The accuracy of the TGA measurements of K West Basin fuel material in moist helium was adequate to compare to the literature data over a range of temperatures. This allowed the data to be assessed at the conditions of primary interest (CVD).

The results from the moist-helium tests, including extrapolations to low temperature, do not exceed the upper bounds of the literature data for that environment at 25°C to 210°C.

The dry-air and moist-air oxidation measurements of the SNF did not provide adequate data or accuracy for comparison with literature data and rate laws at CVD or accident conditions.

Sample fragmentation during TGA testing appears to be more likely at temperatures above 150°C than below that temperature. The samples fragmented in about one-half the tests between 150°C and 350°C. No difference in the tendency for fragmentation could be discerned among the three gas environments tested. While there may be a relationship between sample fragmentation and sample location relative to fuel damage surfaces, there was insufficient data for a conclusion to be made.

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APPENDIX A

ERROR ANALYSIS OF OXIDATION RATE DATA

ERROR ANALYSIS OF OXIDATION RATE DATA

A.1 INTRODUCTION

Reaction rate measurements of SNF stored in the K Basins have been performed using TGA equipment. The small-sample tests were performed in dry air and moist helium under isothermal conditions over a range of temperatures. The results of these tests were reported by Abrefah et al. (1998 and 1999). The tests were performed in support of the SNF Project with the purpose of determining if the reaction kinetics of the K Basin fuel are significantly different from that reported in the literature. If they are not different, the reaction rate equations from the literature will be used to model the fuel. The following analysis evaluates the measurement errors and uncertainties on these data. Only data from samples taken from damaged regions of the fuel were evaluated. Tests were also made in moist air but are not evaluated here.

A.2 BACKGROUND

Reaction kinetics testing in dry air was completed in 1997 using small samples sectioned from two K West Basin-stored, N Reactor-irradiated fuel elements. Seventeen tests used samples from the damaged regions of the two elements (Abrefah et al., 1998). The tests were performed at 69°C to 400°C. Weight-gain data for seven of the tests were judged to follow typical metallic material oxidation kinetics (Abrefah et al 1998). The linear reaction rate was evaluated with a linear regression fit to the linear most portion of each of the useable data curves. Sample and test data relating to these evaluations are listed in Table A.1. The remaining dry-air tests exhibited erratic behavior and were not used for reaction rate data. The erratic data were due to sample material loss and equipment malfunctions during the tests (Abrefah et al. 1998).

Reaction kinetics testing of K Basin fuel samples in moist-helium was completed in 1999. Reaction rate data were obtained from seventeen tests of damaged fuel (Abrefah et al., 1999). Eight of these tests exhibited periods of weight loss, causing them to be of limited value. Linear kinetics were observed for all tests except during the periods of weight loss. Weight loss was determined to be due to loss of oxide products from the sample cup. Data relating to the evaluation of reaction rates from the moist-helium tests are listed in Table A.2.

Table A.1. Oxidation Tests of K Basin Fuel in Dry Air.

TGA Run	Temperature (°C)	Surface Area (cm ²)	Weight Gain* (mg)	Time Span* (h)	Rate Constant (mg/cm ² -h)
51	69	2.41	4.5	70	0.0278
49a	90	2.41	0.3	16.7	0.0066
49b	124	2.39	4.0	8.63	0.182
19a	200	2.56	7.5	4.83	0.576
47	225	2.29	15	4.83	1.26
20	250	2.50	16	2.33	2.62
48	275	2.62	30	4.83	2.47

*Weight gain and time span are for test period over which the oxidation rate slope was calculated.

Table A.2. Oxidation Tests of K Basin Fuel in Moist Helium.

TGA Run	Temperature (°C)	Pressure (kPa)	Surface Area (cm ²)	Weight Gain* (mg)	Time Span* (h)	Rate Constant (mg/cm ² -h-P ^{1/2})	Total Error on Rate Constant
93	76	7.2	1.68	0.35	15.0	0.0053	0.0146
94	77	6.5	1.70	1.5	95.0	0.0042	0.0133
95	78	6.3	1.79	1.9	96.7	0.0040	0.0102
85	98	5.8	2.04	1.2	50.0	0.0049	0.0105
84	99	5.6	1.16	0.5	7.7	0.0262	0.0375
83	100	5.7	1.08	0.8	10.0	0.0303	0.0298
92	105	7.3	1.48	1.6	46.7	0.0090	0.0136
98	129	6.8	1.18	6.5	48.3	0.0448	0.0183
86	133	6.1	1.94	1.9	13.3	0.0301	0.0148
91	134	7.2	1.46	3.4	38.3	0.0184	0.0112
82	160	5.8	1.94	36	45.0	0.1772	0.0278
80	161	5.7	1.24	33	45.0	0.2574	0.0411
81	161	7.6	1.59	3	3.3	0.1903	0.0480
88	162	7.4	1.51	1.75	4.7	0.0964	0.0381
89	163	7.2	1.55	11	45.0	0.0678	0.0173
96	211	7.2	1.79	13	8.0	0.3373	0.0518
97	211	6.7	1.11	7.2	8.0	0.3258	0.0569

A.3 ANALYSIS

Approach

Oxidation rate constants (k) at a given temperature are determined by measuring the rate of weight gain per sample unit area such that

$$k = m/(A*t) \quad (A.1)$$

where m is the weight gain (mg), A is the sample surface area (cm²), and t is time (h). In the case of an oxygen-free moist environment, the water vapor pressure (P) increases the rate in proportion to the square root of P. The reaction rate is normalized to pressure for the rate constant,

$$k^* = m/(A*t*P^{1/2}).$$

If it is assumed that the errors in determining or measuring weight gain, surface area, time and vapor pressure are random and unrelated, the error on k will then propagate approximately as follows:

$$RE^2(k^*) = RE^2(m) + RE^2(A) + RE^2(t) + RE^2(P)/4 \quad (A.2)$$

Where RE(i) is the relative error for parameter i

$$RE(k) = \text{error}(k)/k$$

$$RE(m) = \text{error}(m)/m$$

$$RE(A) = \text{error}(A)/A$$

$$RE(t) = \text{error}(t)/t$$

$$RE(P) = \text{error}(P)/P.$$

Assumptions

Geometric surface area was calculated from micrometer measurements of the sample dimensions. Uncertainty on the area is due primarily to dimensional irregularities and is conservatively estimated to be $\pm 10\%$, thus $RE(A) = 0.1$.

The measurements of time should be within a few seconds per hour but is conservatively estimated at $\pm 1\%$, $RE(t) = 0.01$

Vapor pressure was monitored using a moisture sensor and was stable within about ± 0.5 kPa, and since the measurements were made in range of 5.5 kPa to 7.5 kPa, $RE(P) = 0.1$

The error on weight gain measurement is due to balance calibration accuracy as well as reproducibility, stability, and drift of the balance. Calibration was maintained within 1% at full scale, and since two measurements are required for weight change, $RE(m_c) = 0.02$. Balance stability and drift were assessed with blank runs under moist-helium conditions (Figures A.1 and A.2). Under moist-helium, low-temperature conditions at 75°C , oscillation was ± 0.6 mg and drift was 0.05 mg/h. The drift appeared to decrease with increasing temperature, but was assumed to be constant. Thus, the moist-helium relative error for weight gain in moist helium is given by

$$RE^2(m) = RE^2(m_c) + RE^2(0.6/m) + RE^2(0.05 \cdot t/m).$$

Dry air blank runs were not performed during the period that dry-air testing was done. Thus, balance stability and drift for the dry-air tests are unknown, and the error on weight-gain measurements could not be determined.

The error on sample temperature measure needs to be considered when comparing the reaction rate data to the literature review data. Temperature is also an important parameter when determining the rate law from the data. Sample temperature was determined from a thermocouple placed on the sample cup near the sample. The thermocouple temperature has been shown to be within 10 degrees Celsius of the sample temperature (Cramer and Abrefah 1997), and the recorded temperature typically varied one to two degrees around the set point. Temperature error is therefore assumed to be $\pm 10^\circ\text{C}$.

A summary of the errors used in this analysis is shown in Table A.3.

Table A.3. Errors Assumed in the Evaluation of Relative Error (RE) for Reaction Rate Measurements.

Measurement	Dry Air	Moist Helium
Balance Calibration (RE)	0.02	0.02
Balance Stability (Error)	na*	0.6 mg
Balance Drift (Error)	na*	0.05 mg/hour
Surface Area (RE)	0.1	0.1
Time (RE)	0.01	0.01
Pressure (RE)	N/A	0.1
Temperature (Error)	10°C	10°C

*na = Not available.

A.4 REACTION RATE MEASUREMENTS

Dry Air

The initial stages of oxidation of uranium in dry air are nonlinear with time. At temperatures below 100°C the weight gain has been shown to follow the inverse logarithmic equation, and at higher temperatures the initial stages are parabolic with the final stages become linear (Ritchie 1984).

Figure A.1. Weight Change Data for a Thermogravimetric Analysis Blank Run in Dry then Moist Helium at About 75°C.
Data is shown in relation to Spent Nuclear Fuel Run 95 at the same conditions.

Figure A.2. Weight Change Data for a Thermogravimetric Analysis Blank Run in Moist Helium at about 160°C.

Data is shown in relation to the previous Spent Nuclear Fuel Run 81 at the same conditions. Also shown is Run 81 data minus the blank run data. Note that the Spent Nuclear Fuel run shows periods of samples weight loss after about 400 minutes into the test.

Therefore, to measure the linear oxidation rate the test reaction must be allowed to progress beyond the nonlinear region. If this is not done, the slope of the data curve will yield a reaction rate greater than that in the later, linear stages.

Since the reaction kinetics for uranium follow an Arrhenius relationship, the time required to reach the linear stages of the reaction will increase with decreasing temperature. This assumes that the same reaction mechanism is being observed through the range of temperatures being tested, and that the reaction progress at which the reaction rate is being measured is about the same for each test. Figure A.3 illustrates the reaction progress for a low temperature test compared to a high temperature test, in which the low temperature test was not allowed to progress to the point that the high temperature test did. In this case the low-temperature-measured reaction rate would be at a different reaction progress than the rate measured at high temperature. Hence, an Arrhenius relationship would not be observed.

Figure A.4 shows the estimated time to reach a consistent reaction progress as a function of time when compared to dry-air test TGA Run 20 at 250°C. This analysis indicates that 10⁶ minutes may be needed at 69°C to provide data comparable to the 250°C test. Compare this to the 4600 minutes of test time for dry-air TGA Run 51 at 69°C.

While these are only order-of-magnitude estimates, the large difference between the estimated required time and the actual test time creates an uncertainty for the test. One cannot be certain that the low temperature K Basin fuel tests were tested for sufficient time for an Arrhenius analysis of the SNF reaction rate data. Also, the low temperature data cannot be compared to the literature data, which is presumed to represent linear kinetics.

This analysis does not say that the low temperature data are not valid or that the SNF linear rates are not higher than the literature rates. It only indicates an uncertainty that reduces confidence in the data.

Moist-Helium Tests

The oxidation kinetics of unirradiated uranium in oxygen-free moisture is generally observed to be essentially linear between 20°C and 800°C (Pearce 1989). For this reason test time is not as critical a consideration as with dry air, especially at low temperature. The primary concern is for the reaction to progress sufficiently so that the observed weight gain may be accurately measured.

A.5 RESULTS AND DISCUSSION

Dry-Air Data

Error analysis of the dry-air data could not be performed due to incomplete information about weight measurement accuracy. Drift in the TGA balance was unknown because blank-run data were not available for dry-air testing conditions. Dry-helium blanks were run, but the data were taken during the moist-helium testing and may not have represented the TGA system conditions during dry-air testing. Uncertainties in weight-gain measurements, of which drift was a major

component, were found to be a very significant contributor to the uncertainty in the rate constant for moist-helium tests. Thus, an error analysis of the dry-air data would not be appropriate without an understanding of the balance drift during the time of the tests and therefore, was not done.

Reaction progression considerations for the dry-air tests are discussed in Section A.4. From that perspective the dry-air tests at low temperature (below 150°C) may not have been long enough to measure the linear reaction rate. This may account for the data being higher than the literature data, but the uncertainty is too large to make a conclusion about comparability with literature rates.

Moist-Helium Data

The moist-helium data, plotted in Figure A.5 with error bars and compared to the literature review data, show that the low-temperature data have the greatest uncertainty. With the exception of five data the error bars do not extend above the mean literature rate, and the errors that do extend above the mean are well within the upper prediction interval for the literature data.

Since oxidation in moist-inert gas is generally linear with time, the main consideration for test time is to obtain sufficient weight gain to get an accurate measurement. The effects of the magnitude of balance drift and instability were evaluated in sensitivity analyses. In general the errors on the moist helium data were due primarily to low rate-of weight-gain relative to the measured balance drift and were not due to low total weight gain. Thus, it would be unlikely to improve the measurements with longer tests unless the drift could be shown to be lower than assumed in these analyses.

While the data at 75°C and 100°C are very uncertain, the error analysis does provide an upper bound at these temperatures. This error-bar upper bound indicates that the data do not exceed the literature data.

Figure A.3. Schematic Parabolic Reaction Rate Behavior for the Dry Air Oxidation of Uranium
High temperature reaction rates correspond to a higher reaction progress than low temperature rates.

Figure A.4. Estimated Reaction Times to Reach the Same Reaction Progress at the Indicated Temperature if 200 Minutes are Required at 250°C
The activation energy for the dry-air literature review data was used (Abrefah et al., 1998).

Figure A.5. Data and Error Bars for Spent Nuclear Fuel Tests in Moist Helium.
Unirradiated fuel data shown for reference.

A.6 REFERENCES

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APPENDIX B

OXYGEN EFFECT ON MOIST INERT GAS OXIDATION

OXYGEN EFFECT ON MOIST INERT GAS OXIDATION

B.1 INTRODUCTION

The kinetics of oxidation of uranium in water vapor is significantly affected by a small amount of free oxygen in the carrier gas. These effects have been studied by Colmenares (1985) and are shown in Figure B.1. This is an evaluation of the effects of potential oxygen contamination in the moist helium testing of K Basin fuel (SNF) using TGA equipment.

B.2 BACKGROUND

Samples of K Basin fuel have been tested in moist helium to provide reaction rate data for the SNF Project (Abrefah 1999). It was determined that due to test equipment limitations, air may have been allowed into the test environment. The most likely source of infiltration was from the balance chamber enclosure, which is down stream of the test chamber and near the gas outlet. Other sources of in-leakage were also possible and were not ruled out. Oxygen levels of about 30 ppm to about 80 ppm were measured at the gas flow outlet from the TGA within the range of gas flow used for SNF testing. The oxygen concentration decreased with increasing flow with levels averaging about 80 ppm at 100 cc/min.

The flow of the SNF oxidation test atmosphere was from 70 cc/min to 200 cc/min with 5.5 kPa to 7.5 kPa moisture. The data from these tests are shown in Figure B.2 relative to the spread of the literature review data for unirradiated uranium from Trimble (1998). Most of the SNF data lie somewhat below the mean literature data, and many of them are below the lower prediction interval. Some of these data represent incomplete tests due to loss of reaction product from the sample cup.

B.3 ANALYSIS

Figure B.1 illustrates the effect of oxygen on the reaction rate of uranium in moist-inert gas at 100 °C (Colmenares 1985). Using the 8-kPa data in Figure B.2, the reaction rate is reduced relative to the lowest oxygen levels (<25 ppm) by a factor of about 7 to 8. The highest and lowest rates and the intermediate point at about 45 ppm oxygen are plotted on Figure B.2. Note that the high-oxygen-level rate lies within the scatter of the SNF data at 100 °C. Figure B.1 also illustrates that the effect increases with increasing water vapor pressure, thus the 8-kPa data should be slightly conservative in its effect relative to the SNF data at 5.5 kPa to 7.5 kPa. The data in Figure B.1 do not show the effect of temperature on the oxygen poisoning, but the effect is not expected to be large. Oxygen at 80 ppm will probably be somewhat less than the maximum effect.

The SNF data times 8, the ratio of maximum to minimum oxygen effect, is shown relative to the literature data in Figure B.3. Most of the adjusted SNF data lie below the 95% prediction interval for the literature data. Those that do not are primarily from fragmented samples and incomplete data curves.

Conservatism on the data adjustment in Figure B.3 includes

- The water vapor pressure of the SNF tests is lower than that of the Colmenares data used to derive the adjustment factor of eight. A lower vapor pressure should give a smaller factor.
- The factor of eight was derived assuming oxygen contamination of >150 ppm compared to the maximum measured oxygen of about 80 ppm. Oxygen at 80 ppm would reduce the rates by a smaller factor.
- The oxygen measurement was made well downstream of the sample test chamber and near the suspected major source of air in-leakage path(s). The direction of gas flow relative to the source of oxygen would likely reduce the oxygen at the test sample to below that measured.

This analysis assumes applicability and accuracy of the Colmenares data.

B.4 CONCLUSIONS

- Oxygen in the sample cup during moist-helium testing of SNF did not exceed about 80 ppm and may have been less.
- Most reaction rate data for SNF in moist helium, when adjusted for the maximum effect of oxygen poisoning, did not exceed the literature review data for unirradiated uranium.

B.5 REFERENCES

- Abrefah, J., and R. L. Sell, 1999, *Oxidation of K West Basin Spent Nuclear Fuel in Moist Helium Atmosphere*, PNNL-12167, Pacific Northwest National Laboratory, Richland, Washington.
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Figure B.1. Effect of Oxygen Concentration on the Uranium-Water Vapor Reaction at 100°C.
Total pressure = 101 kPa
(Figure 31 from Colmenares 1985).

Figure B.2. Oxidation of K Basin Fuel in Water Vapor

Figure B.3. Effect of Oxygen on Oxidation in Water Vapor.

APPENDIX C

OXIDATION TEST SAMPLE FRAGMENTATION

OXIDATION TEST SAMPLE FRAGMENTATION

C.1 INTRODUCTION

Oxidation testing of K Basin fuel samples in dry air, moist air, and moist helium at elevated temperatures resulted in various degrees of sample deterioration. The testing was performed using TGA equipment. This is a review of the posttest condition of the samples with an evaluation of the test condition(s) that may relate to sample deterioration.

C.2 DATA

A summary of the sample data is shown in Table C.1.

Forty test samples were derived from two K West Basin fuel elements, 4366 and 4378. Cutting diagrams for the elements showing sample location are shown on Figures C.1, C.2, and C.3. All but two of the samples were taken at or near a damaged and corroded surface which had been exposed to storage canister water. In these cases the sample had been prepared by removing a thin slice of fuel at the damaged surface to provide smooth, easily defined test surfaces. The remaining sample locations were one to six sample thicknesses from the damaged surface. In Table C.1 a sample location of 1 indicates the sample was the first and closest sample to the damage surface, a 2 indicates the sample was one sample thickness from the damage, etc. Sample thickness was approximately 3 mm.

Sample posttest conditions are documented in Abrefah et al. (1998) and the attached letter report by Trimble (1999), or from discussions with the experimenter (Abrefah 1999b). The posttest sample condition was categorized according to the severity of sample deterioration. A rating of one indicates that the sample was intact with various amounts of oxide powder but no visible cracking or fracture. A sample with rating of two exhibited cracks with small amounts of oxide powder. A three indicates sample fracture and powder. A category four sample (or large parts of it) appeared to be intact but disintegrated into many small pieces when attempts were made to handle it. In a few cases the sample oxidized to the point that only oxide powder remained and therefore, could not be evaluated.

C.3 RESULTS

The posttest category number was regressed against sample location number and temperature, individually and together. A weak correlation was found with temperature and no correlation with sample location was indicated by the linear regressions.

The following observations were made:

- Samples Tested Below 150°C: Of the fourteen tested, one fragmented. The fragmented sample was from location two, all others were from locations more removed from known damaged effects.
- Samples Tested at or Above 250°C: Eleven were tested and six fragmented. Sample location of the fractured samples ranged from two to five.
- Samples Tested Between 150°C and 250°C: Fourteen were tested and six fragmented, of which four were from locations one or two.
- Samples from Locations 1 and 2: Fourteen were tested, eight fragmented at temperatures of 144°C to 350°C. The six unfragmented samples were tested at 150°C to 300°C.
- Samples from Locations Beyond 2: Twenty six were tested between 69°C and 300°C and four fragmented. The fragmented samples were tested between 225°C and 300°C.
- Sample Environment: Twenty three samples were tested in air (dry and moist) with four below 150°C, thirteen fragmented all of which were above 140°C. Seventeen were tested in moist helium with ten below 140°C, three fragmented all of which were above 140°C.

C.4 CONCLUSIONS

The following are conclusion regarding exposure of small samples of K Basin fuel exposed to an oxidizing atmosphere:

- Samples derived from within 2.5 cm of damaged surfaces and with a test exposure of 150°C and greater may or may not experience some degree of fragmentation. Probabilities of fragmentation appear to be about even.
- Sample exposures above 250°C may have a greater than even chance of fragmentation.
- Samples taken more than two samples away from the fuel damage surface (about 1/2 cm) and exposed below about 150°C do not readily fragment.
- Samples from within 1/2 cm and tested below 150°C may fragment.
- Fragmentation occurred at a rate of about 50% in all gas environments observed when tested at or above 150°C.

Table C.1. Posttest Condition of Reaction Rate Test Samples.

TGA Run	Samples ¹		Test Environment	Temp. (°C)	Posttest Rating	Posttest Condition of Sample
	Number	Location ²				
51	10-S3-A2	3	Dry air	69	1	Intact with pits
49a	10-S3-A3	4	Dry air	90	1	Intact with pits
49b	10-S3-A4	5	Dry air	124	1	Intact with pits
18	10-S3-F2	2	Dry air	144	4	Disintegrated
18b	10-S1-C4	2	Dry air	150	2	Fractured
19a	10-S3-F3	3	Dry air	200	1	Intact, some oxide
20	10-S3-F4	4	Dry air	250	1	Intact, some oxide
21	10-S1-C1	2	Dry air	300	1	Intact with powder
21a	10-S1-C3	2	Dry air	300	4	Disintegrated
22	10-S1-C2	2	Dry air	350	4	Disintegrated
93	5-S1A-J2A3	3	Moist helium	76	1	Intact with powder
94	5-S1A-J2A4	4	Moist helium	77	1	Intact with powder
95	5-S1A-J2A5	5	Moist helium	78	1	Intact with powder
85	5-S1A-J4C	3	Moist helium	98	1	Intact with powder
84	5-S1A-J2B4	4	Moist helium	99	1	Intact with powder
83	5-S1A-J2B3	3	Moist helium	100	1	Intact with powder
92	5-S1A-J1A5	5	Moist helium	105	1	Intact with powder
98	5-S1A-J2B5	5	Moist helium	129	1	Intact with powder
86	5-S1A-J4D	4	Moist helium	133	1	Intact with powder
91	5-S1A-J1A4	4	Moist helium	134	1	Intact with powder
23	5-S1A-E-2-R1A	1	Dry air	150	1	Intact with powder
na	5-S2-F3D	³	Dry air	150	1	Intact
81	5-S1A-J2A2	1	Moist helium	160	2	Fractured
82	5-S1A-J4B	2	Moist helium	160	3	Fractured, coarse powder
80	5-S1A-J2B1	1	Moist helium	161	3	Fractured, coarse powder
88	5-S1A-J1A2	2	Moist helium	162	1	Intact with powder
89	5-S1A-J1A3	3	Moist helium	163	1	Intact with powder
13	5-S1A-E2C	3	Moist air	198	1	Intact with powder
6r	5-S1A-A2A	2	Dry air	200	2	Fractured
6	5-S1A-A2D	4	Dry air	200	nd	Most of sample oxidized
97	5-S1A-J2B2	2	Moist helium	211	1	Intact with powder
96	5-S1A-J2A5	4	Moist helium	211	1	Intact with powder
47	5-S1A-E4E	4	Dry air	225	2	Cracked with powder
29	5-S1A-E2B	2	Moist air	250	1	Intact with powder
na	5-S2-F3C	³	Dry air	250	1	Intact with powder
48	5-S1A-E4D	4	Dry air	275	4	Disintegrated
14	5-S1A-E2D	4	Moist air	299	4	Disintegrated
7	5-S1A-A2C	3	Dry air	300	nd	Converted to powder
30	5-S1A-E3E	5	Moist air	300	4	Disintegrated
15	5-S1A-E3D	4	Moist air	349	2	May be intact, powder

¹Sample numbers beginning with "5" were from K West Element 4378; those beginning with "10" were from K West Element 4366.

²Sample location is number of sample thicknesses from known damage surface; 1 = first sample.

³From mid-element section, far from corrosion front.

nd = No data; sample completely oxidized during test.

Figure C.1. Sectioning Diagram for K West Basin Fuel Element 4366.

C-6

C-6

Figure C.3. Sectioning Diagram for Section S1A-J from K West Basin Fuel Element 4378

SECTIONING OF SAMPLE SFEC5, 4378 S1A-J

APPENDIX D

K BASIN FUEL SAMPLES TESTED IN DRY AIR

K BASIN FUEL SAMPLES TESTED IN DRY AIR

D.1 INTRODUCTION

Seventeen K Basin fuel samples were tested using TGA in a dry-air environment. The samples were cut from two fuel elements that had been recovered from K West Basin storage canister Elements 4366 and 4378 and transported to the hot cell laboratory in containers SFEC-10 and SFEC-5, respectively. Both fuel elements were damaged on one end, causing fuel material to be exposed. The water exposure resulted in significant corrosion of the metallic fuel (see Figure 2.1 in Abrefah et al. 1998). Element 4378 had more damage than did Element 4366. The samples were taken from the damaged end of the elements, but only one sample included corroded surfaces (see Figures 2.3 and 2.4 in Abrefah et al. 1998). Ten samples from Element 4366 were tested and seven from Element 4378. Sample sizes range from 2.9 g to 8.5 g with 1.2 cm² to 3.0 cm² of exposed fuel surface.

The TGA oxidation tests were done isothermally ranging from 69°C to 400°C. The weight gain data from seven of the 17 tests exhibited primarily normal oxidation behavior for metallic uranium. Normal behavior is characterized by a relatively smooth weight gain curve with no substantial weight loss or sharply increasing weight gain. The rate of weight gain typically decreases with time in a parabolic or logarithmic manner becoming linear after sufficient oxide has covered the surfaces.

Results from the remaining ten tests have been judged anomalous and are termed "unusual" due primarily to erratic weight gain behavior (Abrefah et al. 1998). Sudden and rapid weight gain events have been attributed, in part, to sample breakage, which exposed fresh, highly reactive uranium hydride and metal surfaces to the test environment (Abrefah et al. 1998). Interactions between the sample carrier and the sample chamber wall may have also been a factor in the erratic data. In this scenario the TGA electro-balance would stick-and-release indicating slow and then fast weight gain.

The implications of normal versus the anomalous TGA test results are of interest to the SNF Project. Are the abnormal weight gain curves due to sample breakage and/or hydride inclusions causing highly accelerated oxidation rate? Posttest characterization of the physical nature of the samples was performed to help evaluate this question.

D.2 POSTTEST EXAMINATIONS

A brief posttest characterization of the samples is provided in Abrefah et al (1998). In addition those samples that could be located and identified were video taped and hard copy pictures were made from the video.

D.3 RESULTS

Five samples were located and video taped. The samples were all from the normal test group. Photographs from the video characterizing the samples are attached (Figures D.1 through D.5). Table D.1 summarizes the posttest characterization data from PNNL-11786 and the video examinations.

Table D.1. Oxidation Test Sample Data.

TGA Run	Sample ID ¹	Test Temperature	Weight Gain Data	Posttest Characterization	Reference ²
51	10-S3-A2	69 °C	Normal ³	Intact with small surface pits	Appendix C
49a	10-S3-A3	90 °C	Normal	Intact with moderate surface pits	Appendix C
49b	10-S3-A4	124 °C	Normal	Intact with small surface pits	Appendix C
19a	10-S3-F3	200 °C	Normal	Intact with some oxide	*
47	5-S1A-E4E	225 °C	Normal	Cracked with some fines	Appendix C
20	10-S3-F4	250 °C	Normal	Intact with some oxide	*
48	5-S1A-E4D	275 °C	Normal	Rubble	Appendix C
18	10-S3-F2	144 °C	Unusual	Disintegrated	PNNL-11786
18b	10-S1-C4	150 °C	Unusual	Three pieces	PNNL-11786
23	5-S1A-E2-R1A	150 °C	Unusual	Intact, some oxide	*
6	5-S1A-A2D	200 °C	Unusual	Mostly oxidized	*
6r	5-S1A-A2A	200 °C	Unusual	Broken, three or more pieces	*
21	10-S1-C1	300 °C	Unusual	Intact, some oxide	*
21a	10-S1-C3	300 °C	Unusual	Disintegrated	PNNL-11786
7	5-S1A-A2C	300 °C	Unusual	Pulverized	PNNL-11786
22	10-S1-C2	350 °C	Unusual	Disintegrated	PNNL-11786
8	5-S1A-E1A	400 °C	Unusual	Total oxidation	PNNL-11786

¹IDs starting with 10 indicate samples from fuel Element 4366 and with 5 were from Element 4378.

²Appendix C refers to photographs in Appendix C of this document; PNNL 11786 is Abrefah et al., (1998).

³The later 10% of this test exhibited accelerated oxidation that was not normal.

⁴The data plot is normal, however, the sample was judged anomalous due to low density compared to all other samples.

*Personal communication with J. Abrefah, PNNL.

D.4 DISCUSSION

The oxidation rate constant data from PNNL-11786 are shown on an Arrhenius plot on Figure D.6. More than one rate was reported for some of the unusual test results due to the variability of the weight gain curves. In these cases the data are connected with a vertical line on Figure D.6 to show the range of results. The line fit to the Pearce review data (Trimble 1998) is shown on the Figure for reference.

The surfaces of all samples tested at and below 124°C were pitted but remained intact, while samples tested above 250°C disintegrated. Samples tested at temperature between 144°C to 225°C and having posttest visual data exhibited breakage or disintegration. In many cases samples from tests having erratic data were disintegrated or broken, however, samples from tests with normal data curves did not necessarily remain intact.

It would be of interest to know the pretest condition of the samples. Pretest sample cracks may help to explain the posttest condition of some samples. It is known that the samples were in one piece, but there is no documentation of any pretest cracks that may have existed.

D.5 CONCLUSIONS

- Fuel samples exposed to dry air below 125°C remained intact.
- Fuel samples exposed to dry air above about 140°C are likely to become damaged.
- Erratic weight gain may be an indication of sample damage resulting from the test environment.
- Sample breakage and disintegration does not necessarily result in erratic weight gain.

D.6 REFERENCES

Abrefah, J., H. C. Buchanan, W. M. Gerry, W. J. Gray, and S. C. Marschman, 1998, *Dry Air Oxidation Kinetics of K Basin Spent Nuclear Fuel*, PNNL-11786, Pacific Northwest National Laboratory, Richland, Washington.

Trimble, D. J., 1998, *Reaction Rate Constant for Dry Air Oxidation of K Basin Fuel*, Duke Engineering & Services Hanford, Inc., Richland, Washington.

Figure D.1. Posttest Photograph of Fuel Sample 10-S3-A2 Tested in Dry Air at 69°C

Figure D.2. Posttest Photograph of Fuel Sample 10-S3-A3 Tested in Dry Air at 90°C

Figure D.3. Posttest Photograph of Fuel Sample 10-S3-A4 Tested in Dry Air at 124°C

Figure D.4. Posttest Photograph of Fuel Sample 5-S1A-E4E Tested in Dry Air at 225°C

Figure D.5. Posttest Photograph of Fuel Sample 5-S1A-E4D Tested in Dry Air at 275°C

Figure D.6. Oxidation of K Basin Fuel in Dry Air.
Posttest condition of sample indicated where known.

APPENDIX E

**Letter, M. Epstein to M. G. Plys (FAI)
“Concentration of Inward Leaking Oxygen in the TGA Apparatus”**

March 18, 1999, Fauski & Associates, Inc.
Burr Ridge, Illinois

Fauske & Associates, Inc.

DATE: March 18, 1999

TO: M. G. Plys (FAI)
Darrel Duncan, Duke Engineering & Services, Hanford

FROM: M. Epstein *M. Epstein*

SUBJECT: Concentration of Inward Leaking Oxygen in the TGA Apparatus

Oxygen is assumed to be leaking into the TGA apparatus somewhere downstream of the heat shields. The oxygen concentration in this region is assumed to be the measured outlet value and is denoted by the symbol Y_o . We desire to determine the oxygen concentration in the region above the sample crucible due to the upstream diffusion of oxygen. To accomplish this the TGA carrier gas flow system is divided into three conceptual regions involving one-dimensional carrier gas flow (He) and oxygen counter diffusion.

The stacked passages between parallel heat shields and the gaps between the heat shields and the channel wall comprise region 1. The concentration of oxygen at the downstream (bottom) end of this region is the known value Y_o while the upstream end (top) concentration is Y_1 . The flow area, flow velocity and diffusion length for region 1 are, respectively, A_1 , u_1 and L_1 .

Region 2 is the open flow space between the top of the heat shields and the region above the sample crucible. The gap between the crucible and the channel wall is ignored. The downstream oxygen concentration coincides with that at the top of the heat shield region, namely Y_1 . The oxygen concentration at the upstream and (above the sample crucible) is Y_2 , which is the quantity we seek. The geometry and flow parameters pertinent to region 2 are A_2 , u_2 , and L_2 .

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Telefax (630) 986-5481 E-Mail: fai@fauske.com

Finally, region 3 is the gas feed capillary. The oxygen concentration at its downstream outlet end is Y_2 and the oxygen concentration at its upstream inlet end is Y_3 . The region is described parametrically by A_3 , u_3 and L_3 .

The oxygen concentration Y in each region must obey an ordinary differential equation of the form

$$- u_i \frac{dY}{dx} = D \frac{d^2Y}{dx^2} \quad i = 1, 2, \text{ or } 3 \quad (1)$$

where $x = 0$ is the downstream end of the region and $x = L_i$ is the upstream end of the region. Equation (1) describes the diffusion of oxygen against the carrier gas current of velocity u_i . Integration of this equation subject to the boundary conditions

$$Y = Y_{i-1} \quad \text{at} \quad x = 0 \quad (2)$$

$$Y = Y_i \quad \text{at} \quad x = L_i \quad (3)$$

gives

$$Y(x) = Y_{i-1} - (Y_{i-1} - Y_i) \frac{1 - \exp\left(-\frac{u_i x}{D}\right)}{1 - \exp\left(-\frac{u_i L_i}{D}\right)} \quad i = 1, 2, 3 \quad (4)$$

Differentiation of Eq. (4) yields

$$\frac{dY(x)}{dx} = - (Y_{i-1} - Y_i) \frac{u_i}{D} \frac{\exp\left(-\frac{u_i x}{D}\right)}{1 - \exp\left(-\frac{u_i L_i}{D}\right)} \quad i = 1, 2, 3 \quad (5)$$

On physical grounds we know that the upstream directed diffusion fluxes must match each other at the intersection of regions 1 and 2 and at the intersection of regions 2 and 3. Hence

$$DA_1 \left. \frac{dY}{dx} \right|_{x=L_1} = DA_2 \left. \frac{dY}{dx} \right|_{x=0} \quad (6)$$

and

$$DA_2 \left. \frac{dY}{dx} \right|_{x=L_2} = DA_3 \left. \frac{dY}{dx} \right|_{x=0} \quad (7)$$

Combination of Eqs. (5), (6), and (7) gives

$$\begin{aligned} DA_1 (Y_0 - Y_1) \frac{u_1}{D} \frac{\exp\left(-\frac{u_1 L_1}{D}\right)}{1 - \exp\left(-\frac{u_1 L_1}{D}\right)} \\ = DA_2 (Y_1 - Y_2) \frac{u_2}{D} \frac{1}{1 - \exp\left(-\frac{u_2 L_2}{D}\right)} \end{aligned} \quad (8)$$

and

$$\begin{aligned} DA_2 (Y_1 - Y_2) \frac{u_2}{D} \frac{\exp\left(-\frac{u_2 L_2}{D}\right)}{1 - \exp\left(-\frac{u_2 L_2}{D}\right)} \\ = DA_3 (Y_2 - Y_3) \frac{u_3}{D} \frac{1}{1 - \exp\left(-\frac{u_3 L}{D}\right)} \end{aligned} \quad (9)$$

Simplifying Eqs. (8) and (9), and noting that $A_1 u_1 = A_2 u_2 = A_3 u_3$, we obtain

$$(Y_0 - Y_1) \left(\frac{1 - E_1}{E_1} \right) = (Y_1 - Y_2) \frac{1}{E_2} \quad (10)$$

$$(Y_1 - Y_2) \left(\frac{1 - E_2}{E_2} \right) = (Y_3 - Y_2) \frac{1}{E_3} \quad (11)$$

where we introduced the definitions

$$E_1 = 1 - \exp \left(- \frac{u_1 L_1}{D} \right) \quad (12)$$

$$E_2 = 1 - \exp \left(- \frac{u_2 L_2}{D} \right) \quad (13)$$

$$E_3 = 1 - \exp \left(- \frac{u_3 L_3}{D} \right) \quad (14)$$

By solving Eqs. (10) and (11) we get Y_2 :

$$Y_2 = \frac{G Y_0 + Y_3}{1 + G} \quad (15)$$

where

$$G = \frac{E_3(1 - E_1)(1 - E_2)}{E_1 + E_2 - E_1 E_2} \quad (16)$$

Now Y_3 is the oxygen concentration at the entrance to the gas inlet capillary tube. At this remote location relative to the upstream end of the heat shield region it is reasonable to assume $Y_3 = 0$. Also since $u_3 L_3/D \gg 1$ for the gas inlet capillary tube, $E_3 \approx 1.0$. The flow rate through the system is assumed to be 100 cc min^{-1} ($1.7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$). Then the flow velocity in the $1.22 \times 10^{-4} \text{ m}^2$ gaps between the radiation shields and the channel wall is $1.4 \times 10^2 \text{ m s}^{-1}$. The effective gas flow rate through the radiation shield area (region 1) is assigned one-half this value to account for the slower flow between radiation shields; therefore $u_1 = 7 \times 10^3 \text{ m s}^{-1}$. The flow velocity in the wide open region 2 ($A_2 = 5.77 \times 10^{-4} \text{ m}^2$) is $u_2 = 2.95 \times 10^3 \text{ m s}^{-1}$. The lengths of regions 1 and 2 are, respectively, $L_1 = 3.1 \times 10^2 \text{ m}$ and $L_2 = 0.115 \text{ m}$. The He/O₂ binary diffusion coefficient is taken to be the same as that for the H₂/O₂ system at 160°C, or $D = 1.5 \times$

$10^{-4} \text{ m}^2 \text{ s}^{-1}$. Thus, from Eqs. (12) and (13), $E_1 = 0.765$ and $E_2 = 0.895$, and from Eq. (16) we predict an oxygen concentration at the sample crucible (divided by the measured downstream value) of

$$\frac{Y_2}{Y_0} = 0.023$$

In conclusion, the oxygen concentration in gas above the sample crucible is estimated to be about 2% of the measured outlet value for a nominal supply gas flowrate of 100 cc/min, assuming that oxygen enters the apparatus below the heat shields. For example, when 80 ppm O_2 are measured at the outlet, only about 2 ppm O_2 are estimated to be present in gases that can react with the sample.

ME:lak

ANALYTICAL CALCULATIONS

Page 1 of 4Subject Check on FAI "Conc. of Inward Leaking O₂ in TGA"Originator DT Trimble DDT Date 6-26-00

Checker _____ Date _____

Y_0 = Concentration of O₂ at downstream end of region 1 in TGA at gas outlet where O₂ measurements were made.

Y_2 = Oxygen concentration in TGA sample chamber at the outlet from the gas feed capillary. This is the quantity sought by the calculation.

Y_3 = O₂ concentration at the upstream inlet to the gas feed capillary. The capillary tube has length L_3 , cross sectional area A_3 , and flow velocity μ_3 . Y_3 is assumed to have a value of zero (no oxygen at this point).

FROM FAI

$$Y_2 = \frac{GY_0 + Y_3}{1 + G}$$

equ. 15

$$G = \frac{\bar{E}_3(1 + \bar{E}_1)(1 - \bar{E}_2)}{\bar{E}_1 + \bar{E}_2 - \bar{E}_1\bar{E}_2}$$

$$G = \frac{\bar{E}_3(1 - \bar{E}_1)(1 - \bar{E}_2)}{\bar{E}_1 + \bar{E}_2 - \bar{E}_1\bar{E}_2} \quad \text{Eq. 16}$$

where $\bar{E}_i = 1 - \exp\left[-\frac{\mu_i L_i}{D}\right]$ equ. 12, 13, 14

$\mu_i = Q/A_i$ at region i (flow velocity)

$$Q = 100 \text{ cc/min} = 1.67 \times 10^{-6} \text{ m}^3/\text{s}$$

A_i = gas flow area

D = diffusion coefficient

$$= 1.5 \times 10^{-4} \text{ m}^2/\text{s} \quad (\text{assumed by FAI})$$

L_i = diffusion length through region i

ANALYTICAL CALCULATIONS

Page 2 of 4Subject Check of FAI memo on O₂ leakage in TGAOriginator DJ Trimble DJSDate 6-27-00

Checker _____

Date _____

Also given by FAI

$$L_1 = 3.1 \times 10^{-2} \text{ m}$$

$$A_1 = 1.22 \times 10^{-4} \text{ m}^2$$

$$L_2 = 0.115 \text{ m}$$

$$A_2 = 5.77 \times 10^{-4} \text{ m}^2$$

FAI assumed that $\frac{\mu_3 L_3}{D} \gg 1$ and thus $\bar{E}_3 \approx 1.0$ checking this assumption:assume capillary tube length $L_3 = 4'' = 0.1 \text{ m}$ and with diameter $d = 0.03'' = \frac{0.03}{25.4} \text{ m} = 7.6 \times 10^{-4} \text{ m}$

$$\text{Then } A_3 = \frac{\pi}{4} d^2 = 4.6 \times 10^{-7} \text{ m}^2$$

$$\mu_3 = \frac{Q}{A} = \frac{1.67 \times 10^{-6} \text{ m}^3/\text{s}}{4.6 \times 10^{-7} \text{ m}^2} = 3.65 \text{ m/s}$$

$$\frac{\mu_3 L_3}{D} = \frac{3.65 \text{ m/s} (0.1 \text{ m})}{1.5 \times 10^{-4} \text{ m}^2/\text{s}} = 2.4 \times 10^3$$

$$\text{Thus } \bar{E}_3 = 1 - \exp(-2.4 \times 10^3) = 1 - 0.99999 \dots \approx 1.0$$

OR using conservative assumptions

$$L_3 = 1'' = 0.025 \text{ m}, d = 0.25'' = 6.35 \times 10^{-3} \text{ m}$$

$$A_3 = 3.17 \times 10^{-5} \text{ m}^2, \mu_3 = \frac{1.67 \times 10^{-6} \text{ m}^3/\text{s}}{3.17 \times 10^{-5} \text{ m}^2} = 0.053 \text{ m/s}$$

$$\frac{\mu_3 L_3}{D} = \frac{(0.053)(0.025)}{1.5 \times 10^{-4}} = 8.8$$

$$\bar{E}_3 = 1 - \exp(-8.8) = 1 - 1.5 \times 10^{-4} = 0.9998 \approx 1.0$$

ANALYTICAL CALCULATIONS

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Checker _____

Date _____

Checking FAI calculationsFor $Y_3 = 0$ (basic premise)

$$Y_2 = \frac{GY_0 + 0}{1 + G}$$

$$\boxed{Y_2/Y_0 = \frac{G}{1 + G}}$$

For $\bar{E}_2 = 1.0$

$$G = \frac{1(1 - \bar{E}_1)(1 - \bar{E}_2)}{\bar{E}_1 + \bar{E}_2 - \bar{E}_1\bar{E}_2}$$

$$\bar{E}_1 = 1 - \exp\left[-\frac{\mu_1 L_1}{D}\right]$$

using FAI given: $D = 1.5 \times 10^{-4} \text{ m}^2/\text{s}$
 $L_1 = 3.1 \times 10^{-2} \text{ m}$
 $A_1 = 1.22 \times 10^{-4} \text{ m}^2$
 $Q = 1.67 \times 10^{-6} \text{ m}^3/\text{s}$

$$\mu_1 = \frac{Q}{A} = \frac{1.67 \times 10^{-6} \text{ m}^3/\text{s}}{1.22 \times 10^{-4} \text{ m}^2} = 1.37 \times 10^{-2} \text{ m/s}$$

but FAI recommends $\mu_1 = \frac{1}{2} (1.37 \times 10^{-2}) \text{ m/s}$

$$\text{thus } \bar{E}_1 = 1 - \exp\left[-\frac{\frac{1}{2}(1.37 \times 10^{-2}) \text{ m/s} (3.1 \times 10^{-2} \text{ m})}{1.5 \times 10^{-4} \text{ m}^2/\text{s}}\right]$$

$$= 1 - \exp(-3.141) \text{ DON'T } 1 - \exp(-1.4157)$$

$$= 1 - 0.243$$

$$= 0.757$$

ANALYTICAL CALCULATIONS

Page 4 of 4Subject Check of FAI memo on O₂ leakage in TGAOriginator DJ Trimble DJSDate 6-27-00

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Date _____

$$E_2 = 1 - \exp \left[-\frac{\mu_2 L_2}{D} \right]$$

using FAI given: $D = 1.5 \times 10^{-4} \text{ m}^2/\text{s}$
 $L_2 = 0.115 \text{ m}$
 $A_2 = 5.77 \times 10^{-4} \text{ m}^2$
 $Q = 1.67 \times 10^{-6} \text{ m}^3/\text{s}$

$$\mu_2 = \frac{Q}{A_2} = \frac{1.67 \times 10^{-6} \text{ m}^3/\text{s}}{5.77 \times 10^{-4} \text{ m}^2} = 2.89 \times 10^{-3} \text{ m/s}$$

$$E_2 = 1 - \exp \left[-\frac{(2.89 \times 10^{-3} \text{ m/s})(0.115 \text{ m})}{1.5 \times 10^{-4} \text{ m}^2/\text{s}} \right]$$

$$= 1 - \exp(-2.216)$$

$$= 1 - 0.109 = 0.891$$

$$G = \frac{(1-E_1)(1-E_2)}{E_1 + E_2 + E_1 E_2} = \frac{(0.243)(0.109)}{(0.757)(0.891) - 0.757(0.891)}$$

$$= \frac{0.0265}{0.9735} = \frac{0.0265}{\text{DJS}} = 0.0272$$

$$\frac{Y_2}{Y_0} = \frac{G}{1+G} = \frac{0.0272}{1.0272} = \underline{\underline{0.0265}}$$

This is in close agreement
with FAI memo.

DJ Trimble

E-10

6-27-00

APPENDIX F

**LINEAR REGRESSION ANALYSES OF REACTION RATE DATA AND
CALCULATIONS OF CONFIDENCE LIMITS ON THE MEAN OF THE
REGRESSIONS (OCRWM)**

Date: 7-13-00

Performed by
D.J. Trimble

Checked by:
M. J. Packer

F.1 PURPOSE AND OBJECTIVE

The objective of this calculation is to find the 95% confidence limits (CLs) on the true mean value of the regression line for two sets of reaction rate data utilizing an Arrhenius equation model. The data of interest were the rate constants for K Basin SNF and literature review data for unirradiated uranium, reacting in oxygen-free water vapor as a function of temperature and water vapor pressure. The confidence limits would then be used to determine comparability of the two data sets.

F.2 INPUT DATA

The K Basin SNF data are from tests of SNF reacting in moist helium (Abrefah and Sells 1999). Nine of the reported SNF data are used in these analyses and include those tests with "complete data" at temperatures above 90°C. Complete data are those tests that exhibited relatively linear weight gain throughout the test, allowing the reaction rate constant to be evaluated over a wide range of test time. These data are listed in Table F-1.1. The data were not acquired or developed in accordance with an approved Quality Assurance program that meets the OCRWM QARD (DOE/RW-0333P) and have not been qualified in accordance DOE/RW-0333P, making them existing (unqualified) data as defined in DOE/RW-0333P.

The literature review data for the oxidation of unirradiated uranium in oxygen-free water vapor are reported in Trimble (1998). They include 241 data gathered from 19 sources, and are listed in Table F-2.1. They are existing (unqualified) data as defined in DOE/RW-0333P.

F.3 SUMMARY

The 95% CLs were calculated for the linear regressions of two sets of reaction rate data sets: K Basin SNF and unirradiated uranium. This was done by first regressing Arrhenius transformations of the data obtaining the line fit for $\log k'$ versus $1/T$, where k' is reaction rate constant divided by square root of water vapor pressure and T is absolute temperature. The confidence limits were then calculated for the true mean values of the regressions. Those limits were compared in Figure F-1, showing that the SNF data do not, on average, exceed the literature review data for unirradiated uranium.

F.4 ASSUMPTIONS

No assumptions were used in these calculations.

F.4 SOFTWARE APPLICATIONS

All calculations were performed using spreadsheet software Microsoft Excel® version 5.0 on Hanford PC #WC64916. This work was originally done in the year 1999 and then checked in 2000.

The linear regression coefficients, intercept and slope, and the standard error on the regression were calculated using the Excel Regression Analysis Tool. Spreadsheet formulas were written to calculate the confidence limits on the true mean value of the regressions.

F.5 CALCULATIONS

F.5.1 Regression Analyses

The linear regression line for a set of x,y data can be obtained using the method of least squares. This analysis is used to calculate the regression coefficients, a and b, for the equation $y = a + b \cdot x$. A value for x, X_0 , can be then used to predict a y value, Y_{hat} such that $Y_{\text{hat}} = a + b \cdot X_0$; with a standard error of prediction, se. The following equations are used in the regression analysis:

$$\begin{aligned} a &= S_{xy}/S_{xx} \\ b &= \text{aveY} - a \cdot \text{aveX} \\ \text{se}^2 &= SS_{\text{resid}}/(n-2). \end{aligned}$$

Where:

$$\begin{aligned} n &= \text{the number of observations (data),} \\ \text{aveY} &= \text{mean value for } Y_i, \\ \text{aveX} &= \text{mean value for } X_i, \\ S_{xy} &= \text{sum}(X_i \cdot Y_i) - n \cdot \text{aveY} \cdot \text{aveX}, \\ S_{xx} &= \text{sum}(X_i - \text{aveX})^2, \\ SS_{\text{resid}} &= \text{sum}(Y_i - Y_{\text{hat}})^2, \\ Y_{\text{hat}} &= a + b \cdot X_i. \end{aligned}$$

The regression analysis input consisted of transformed reaction rate data such that $X_i = 1/T_i$ and $Y_i = \log k'_i$, where T is the temperature of the reaction in degrees K, $k' = k/P^{0.5}$, k is the reaction rate constant in weight gain per unit area, mg/cm²-h, and P is the water vapor pressure of the reaction gas in kPa.

The Excel Summary Output for the regression of the SNF data is displayed in Table F-1.3, and Summary Output for the regression of the literature review data is displayed in Table F-2.3.

F.5.2 Confidence Limits

The following equations were used to calculate the 95% confidence limits on the true mean value of the data as predicted by the regression coefficients:

$$CL = Y_{\text{hat}} \pm t * SdtErrP$$

Where:

$$Y_{\text{hat}} = a + b * X_0,$$

t = t-distribution statistic at $p = 0.05$ with $n-2$ degrees of freedom,

$$SdtErrP = se[1/n + (X_0 - \text{aveX})^2/S_{xx}]^{1/2},$$

aveX = mean value of the X data, and

$$S_{xx} = \sum (X_i - \text{aveX})^2$$

X_0 = predictor variable.

The results of the spreadsheet calculations of the confidence limits on the true mean value of the SNF data are shown in Table F-1.4. The upper and lower CLs were calculated for the temperature range 20°C to 220°C.

The results of the spreadsheet calculations of the CLs on the true mean value of the literature review data are shown in Table F-2.4. The upper and lower CLs were calculated for the temperature range 20°C to 220°C.

F.6 RESULTS

The 95% CLs on the mean values of two sets of reaction rate data, K Basin SNF and literature review data, were calculated from the regression coefficients. The CLs for both data sets are plotted on Figure F-1 providing a means for judging the comparability of the data.

F.7 CONCLUSIONS

The 95% CLs on the mean of the reaction rate data for K Basin SNF and unirradiated uranium in oxygen-free water vapor are shown in Figure F-1. A graphical comparison of the line plots shows that the SNF data do not exceed the literature view data for unirradiated uranium within the temperature range 25°C to 210°C.

F.8 REFERENCES

- Abrefah, J, and R. Sell, 1999, *Oxidation of K West Basin Spent Nuclear Fuel in Moist Helium Atmosphere*, PNNL-12167, Pacific Northwest Laboratory, Richland, Washington.
- Trimble, D. J., 1998, *Reaction Rate Constant for Uranium in Water and Water Vapor*, HNF-2853, Rev. 0, Duke Engineering & Services Hanford, Inc., Richland, Washington.

Table F-1.1. Reaction Rate Data for SNF in Moist Helium.

TEST RUN	TEMPERATURE (T)		pressure(P) kPa	RATE Constant**		comment
	C	K		k, mg/cm ² -h	k', mg/cm ² -hr-kPa ^{0.5}	
TGA 85	98	371	5.8	0.0118	4.8997E-03	complete data
TGA 89	163	436	7.2	0.1819	6.7790E-02	complete data
TGA 91	134	407	7.2	0.0493	1.8373E-02	complete data
TGA 92	105	378	7.3	0.0243	8.9938E-03	complete data
TGA 80	161	434	5.7	0.6145	2.5739E-01	complete data
TGA 82	160	433	5.8	0.4268	1.7722E-01	complete data
TGA 96	211	484	7.2	0.9050	3.3727E-01	complete data
TGA 97	211	484	6.7	0.8430	3.2568E-01	complete data
TGA 98	129	402	6.8	0.1169	4.4829E-02	complete data

$$*T(K) = T(C) + 273$$

**Data were selected from Table 3.1 of Abrefah and Sells (1999) using only data from tests run above 90°C with results having "complete data." Complete data are those results that exhibited linear weight gain throughout the test.

Table F-1.2. Spreadsheet Output of Statistical Calculations of Transformed SNF Reaction Rate Data in Table F-1.1.

		1/T (K ⁻¹)	log k'				
obs.	test	X	Y	X*Y	(X-aveX) ²	Yhat	(Y - Yhat) ²
1	TGA 85	0.0026954	-2.3098	-6.226E-03	1.0627E-07	-2.15710	0.023326
2	TGA 89	0.0022936	-1.1688	-2.681E-03	5.7542E-09	-0.99096	0.031638
3	TGA 91	0.0024570	-1.7358	-4.265E-03	7.6681E-09	-1.46522	0.073223
4	TGA 92	0.0026455	-2.0461	-5.413E-03	7.6214E-08	-2.01225	0.001143
5	TGA 80	0.0023041	-0.5894	-1.358E-03	4.2624E-09	-1.02164	0.186814
6	TGA 82	0.0023095	-0.7515	-1.736E-03	3.5959E-09	-1.03708	0.081561
7	TGA 96	0.0020661	-0.4720	-9.752E-04	9.2002E-08	-0.33087	0.019923
8	TGA 97	0.0020661	-0.4872	-1.007E-03	9.2002E-08	-0.33087	0.024443
9	TGA 98	0.0024876	-1.3484	-3.354E-03	1.3954E-08	-1.55391	0.042216
average of column>		0.0023694 =aveX	-1.2121 =aveY				
sum of column>				-2.701E-02 =sumX*Y	4.0172E-07 =S _{xx}		0.48429 =SS _{resid}

Table F-1.3. Output from Excel Regression of the SNF Reaction Rate Data.

Table F-1S: Output from Excel Regression of the SNT Reaction Rate Data.

SUMMARY OUTPUT						
Regression Statistics		USED MICROSOFT EXCEL version 5.0 on Hanford PC #WC64916				
Multiple R	0.9353124					
R Square	0.8748092					
Adjusted R Square	0.8569248	where $X=1/T(K^{-1})$ and $Y=\log k'$ as shown in Table F-1.2.				
Standard Error (se)	0.263026					
Observations	9					
ANOVA						
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>	
Regression	1	3.3840461	3.384046	48.91466	0.0002127	
Residual	7	0.4842786	0.069183			
Total	8	3.86832473				
	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95.0%</i>
Intercept	5.6649	0.98719	5.7384	0.000707	3.33059	7.99927
X Variable 1(slope)	-2902.40	414.990	-6.9939	0.000213	-3883.7	-1921.1

result: $\log k' = 5.665 - 2902.40*(1/T)$ with std error (se) = 0.2630

Table F-1.4. Spreadsheet Output for the Calculation of 95% Confidence Limits on the True Mean Value of the Regression of SNF Reaction Rate Data.

Temp	X			Y (log k')			k' (mg/cm ² -hr-kPa ^{0.5})		
(C)	1/T ₀ (K ⁻¹)	(X ₀ -aveX) ²	stdErrP	Y-hat	lower CL*	upper CL	lower CL	mean	upper CL
220	2.028E-03	1.163E-07	0.16648	-0.2214	-0.6151	0.1723	2.43E-01	6.01E-01	1.49E+00
200	2.114E-03	6.516E-08	0.13751	-0.4703	-0.7955	-0.1451	1.60E-01	3.39E-01	7.16E-01
180	2.208E-03	2.622E-08	0.11047	-0.7412	-1.0024	-0.4800	9.95E-02	1.81E-01	3.31E-01
160	2.309E-03	3.596E-09	0.09114	-1.0371	-1.2526	-0.8216	5.59E-02	9.18E-02	1.51E-01
140	2.421E-03	2.691E-09	0.09028	-1.3616	-1.5751	-1.1482	2.66E-02	4.35E-02	7.11E-02
120	2.545E-03	3.066E-08	0.11387	-1.7192	-1.9885	-1.4500	1.03E-02	1.91E-02	3.55E-02
100	2.681E-03	9.705E-08	0.15621	-2.1152	-2.4845	-1.7458	3.28E-03	7.67E-03	1.80E-02
80	2.833E-03	2.148E-07	0.21136	-2.5560	-3.0557	-2.0562	8.80E-04	2.78E-03	8.79E-03
60	3.003E-03	4.014E-07	0.27716	-3.0497	-3.7051	-2.3943	1.97E-04	8.92E-04	4.03E-03
40	3.195E-03	6.814E-07	0.35360	-3.6066	-4.4427	-2.7704	3.61E-05	2.47E-04	1.70E-03
20	3.413E-03	1.089E-06	0.44184	-4.2394	-5.2842	-3.1946	5.20E-06	5.76E-05	6.39E-04

Input: $Y_{\text{hat}} = 5.665 - 2902/T$,
 $n = 9$,
 $t(0.05, 5) = 2.3646$,
 $\text{aveX} = 0.0023694$,
 $\text{se} = 0.2630$,
 $S_{xx} = 4.0172E-7$.

Table F-2.1. Literature Review Data for Oxidation of Uranium in Oxygen-Free Moist Gas (Trimble 1998). Page 1 of 6.

obs.	TEMPERATURE		P of H ₂ O	rate constant	k'	REFERENCE*
	(C)	(K)	(kPa)	k, mg/cm ² /hr	mg/cm ² /h/kPa ^{0.5}	
1	65	338	25.00	0.09100	1.82E-02	Baker et al (1964)
2	80	353	47.34	0.2330	3.39E-02	Baker et al (1964)
3	100	373	3.32	0.05900	3.24E-02	Baker et al (1964)
4	100	373	6.64	0.08600	3.34E-02	Baker et al (1964)
5	100	373	13.30	0.1100	3.02E-02	Baker et al (1964)
6	100	373	26.60	0.1500	2.91E-02	Baker et al (1964)
7	100	373	53.15	0.2000	2.74E-02	Baker et al (1964)
8	100	373	79.70	0.3490	3.91E-02	Baker et al (1964)
9	100	373	93.00	0.3410	3.54E-02	Baker et al (1964)
10	100	373	101.0	0.6380	6.35E-02	Baker et al (1964)
11	80	353	47.17	0.1277	1.86E-02	Baker et al (1965)
12	100	373	0.61	0.01344	1.73E-02	Besson and Santon (1963)
13	62	335	7.97	0.02400	8.50E-03	Colmenares (1984)
14	80	353	7.97	0.04500	1.59E-02	Colmenares (1984)
15	100	373	0.007	0.005500	6.82E-02	Colmenares (1984)
16	100	373	0.012	0.007000	6.39E-02	Colmenares (1984)
17	100	373	0.070	0.007500	2.83E-02	Colmenares (1984)
18	100	373	0.30	0.03000	5.48E-02	Colmenares (1984)
19	100	373	1.50	0.05500	4.49E-02	Colmenares (1984)
20	100	373	3.00	0.08500	4.91E-02	Colmenares (1984)
21	100	373	5.00	0.1200	5.37E-02	Colmenares (1984)
22	100	373	8.50	0.1400	4.80E-02	Colmenares (1984)
23	100	373	8.50	0.1600	5.49E-02	Colmenares (1984)
24	100	373	13.30	0.1670	4.58E-02	Colmenares (1984)
25	100	373	13.30	0.2170	5.95E-02	Colmenares (1984)
26	100	373	13.30	0.2250	6.17E-02	Colmenares (1984)
27	100	373	13.30	0.2300	6.31E-02	Colmenares (1984)
28	100	373	13.30	0.2400	6.58E-02	Colmenares (1984)
29	25	298	4.52	0.003226	1.52E-03	Corcoran et al. (1965)
30	40	313	3.19	0.005781	3.24E-03	Corcoran et al. (1965)
31	40	313	2.33	0.004571	3.00E-03	Grimes and Morris (1965)
32	199	472	101.0	3.424	3.41E-01	Hayward et al.(1994)
33	199	472	101.0	4.868	4.84E-01	Hayward et al.(1994)
34	200	473	101.0	4.962	4.94E-01	Hayward et al.(1994)
35	201	474	101.0	2.991	2.98E-01	Hayward et al.(1994)
36	201	474	101.0	3.070	3.05E-01	Hayward et al.(1994)
37	201	474	101.0	3.231	3.21E-01	Hayward et al.(1994)
38	250	523	101.0	20.26	2.02E+00	Hayward et al.(1994)
39	250	523	101.0	23.78	2.37E+00	Hayward et al.(1994)
40	252	525	101.0	10.07	1.00E+00	Hayward et al.(1994)
41	252	525	101.0	10.69	1.06E+00	Hayward et al.(1994)
42	285	558	101.0	38.20	3.80E+00	Hayward et al.(1994)
43	285	558	101.0	41.96	4.18E+00	Hayward et al.(1994)
44	160	433	101.0	1.200	1.19E-01	Hopkinson (1959)

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obs.	TEMPERATURE		P of H2O	rate constant	k'	REFERENCE*
	(C)	(K)	(kPa)	k, mg/cm ² /hr	mg/cm ² /h/kPa ^{0.5}	
45	200	473	101.0	4.800	4.78E-01	Hopkinson (1959)
46	200	473	101.0	6.000	5.97E-01	Hopkinson (1959)
47	200	473	101.0	6.000	5.97E-01	Hopkinson (1959)
48	230	503	101.0	18.00	1.79E+00	Hopkinson (1959)
49	230	503	101.0	18.00	1.79E+00	Hopkinson (1959)
50	230	503	101.0	96.00	9.55E+00	Hopkinson (1959)
51	250	523	101.0	54.00	5.37E+00	Hopkinson (1959)
52	250	523	101.0	96.00	9.55E+00	Hopkinson (1959)
53	250	523	101.0	96.00	9.55E+00	Hopkinson (1959)
54	270	543	101.0	102.0	1.01E+01	Hopkinson (1959)
55	270	543	101.0	114.0	1.13E+01	Hopkinson (1959)
56	270	543	101.0	114.0	1.13E+01	Hopkinson (1959)
57	200	473	101.0	14.05	1.40E+00	Huddle (1953)
58	250	523	101.0	79.83	7.94E+00	Huddle (1953)
59	100	373	1.59	0.1761	1.39E-01	Jackson and Condon (1977)
60	100	373	2.86	0.2110	1.25E-01	Jackson and Condon (1977)
61	150	423	0.40	0.07798	1.24E-01	Jackson and Condon (1977)
62	150	423	1.59	0.3253	2.58E-01	Jackson and Condon (1977)
63	150	423	2.86	0.4060	2.40E-01	Jackson and Condon (1977)
64	75	348	4.39	0.02258	1.08E-02	Kondo (1964)
65	75	348	5.32	0.01747	7.58E-03	Kondo (1964)
66	75	348	7.97	0.02554	9.05E-03	Kondo (1964)
67	75	348	10.63	0.03495	1.07E-02	Kondo (1964)
68	75	348	13.28	0.04302	1.18E-02	Kondo (1964)
69	80	353	0.40	0.03361	5.33E-02	Kondo (1964)
70	80	353	1.59	0.07394	5.86E-02	Kondo (1964)
71	80	353	2.86	0.09277	5.49E-02	Kondo (1964)
72	98	371	0.40	0.04840	7.67E-02	Kondo (1964)
73	60	333	11.03	0.02070	6.23E-03	Kondo (1974)
74	75	348	38.40	0.01142	1.84E-03	Magnani (1974)
75	35	308	5.58	0.008067	3.41E-03	Orman (1963)
76	50	323	12.35	0.02823	8.03E-03	Orman (1963)
77	65	338	24.98	0.09142	1.83E-02	Orman (1963)
78	70	343	31.06	0.04168	7.48E-03	Orman (1963)
79	70	343	31.06	0.04571	8.20E-03	Orman (1963)
80	80	353	47.17	0.2339	3.41E-02	Orman (1963)
81	100	373	101.0	0.6386	6.35E-02	Orman (1963)
82	100	373	0.94	0.02285	2.35E-02	Orman (1964)
83	100	373	1.30	0.05781	5.07E-02	Orman (1964)
84	100	373	2.22	0.06588	4.42E-02	Orman (1964)
85	100	373	2.78	0.06453	3.87E-02	Orman (1964)
86	100	373	3.16	0.09815	5.52E-02	Orman (1964)
87	100	373	23.12	0.2339	4.86E-02	Orman (1964)
88	100	373	41.86	0.2689	4.16E-02	Orman (1964)
89	100	373	50.89	0.2110	2.96E-02	Orman (1964)
90	100	373	56.74	0.3078	4.09E-02	Orman (1964)

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obs.	TEMPERATURE		P of H2O	rate constant	k'	REFERENCE*
	(C)	(K)	(kPa)	k, mg/cm ² /hr	mg/cm ² /h/kPa ^{0.5}	
91	100	373	65.91	0.3522	4.34E-02	Orman (1964)
92	100	373	69.90	0.4678	5.60E-02	Orman (1964)
93	100	373	73.62	0.4275	4.98E-02	Orman (1964)
94	100	373	80.53	0.4625	5.15E-02	Orman (1964)
95	100	373	87.04	0.5055	5.42E-02	Orman (1964)
96	100	373	92.36	0.4315	4.49E-02	Orman (1964)
97	100	373	97.54	0.5310	5.38E-02	Orman (1964)
98	100	373	99.40	0.5781	5.80E-02	Orman (1964)
99	100	373	99.67	0.5835	5.84E-02	Orman (1964)
100	100	373	100.3	0.5620	5.61E-02	Orman (1964)
101	100	373	101.0	0.6386	6.35E-02	Orman (1964)
102	20	293	2.39	0.002420	1.56E-03	Orman and Walker (1964)
103	22	295	2.66	0.002151	1.32E-03	Orman and Walker (1964)
104	22	295	2.66	0.004033	2.47E-03	Orman and Walker (1964)
105	40	313	7.31	0.006050	2.24E-03	Orman and Walker (1964)
106	40	313	7.31	0.01210	4.48E-03	Orman and Walker (1964)
107	50	323	12.35	0.01344	3.82E-03	Orman and Walker (1964)
108	50	323	12.35	0.01478	4.21E-03	Orman and Walker (1964)
109	60	333	19.80	0.02420	5.44E-03	Orman and Walker (1964)
110	70	343	31.09	0.04168	7.48E-03	Orman and Walker (1964)
111	70	343	31.09	0.04168	7.48E-03	Orman and Walker (1964)
112	74	347	36.81	0.05109	8.42E-03	Orman and Walker (1964)
113	74	347	36.81	0.05109	8.42E-03	Orman and Walker (1964)
114	105	378	20.80	0.01500	3.29E-03	Pearce and Kay (1987)
115	105	378	78.50	0.2380	2.69E-02	Pearce and Kay (1987)
116	105	378	100.0	0.4000	4.00E-02	Pearce and Kay (1987)
117	150	423	5.10	0.2800	1.24E-01	Pearce and Kay (1987)
118	150	423	20.80	0.4400	9.65E-02	Pearce and Kay (1987)
119	150	423	20.80	0.5100	1.12E-01	Pearce and Kay (1987)
120	150	423	49.30	0.7200	1.03E-01	Pearce and Kay (1987)
121	150	423	49.30	0.7500	1.07E-01	Pearce and Kay (1987)
122	150	423	49.30	0.7700	1.10E-01	Pearce and Kay (1987)
123	150	423	78.50	1.260	1.42E-01	Pearce and Kay (1987)
124	180	453	49.30	1.820	2.59E-01	Pearce and Kay (1987)
125	180	453	49.30	1.870	2.66E-01	Pearce and Kay (1987)
126	180	453	78.50	1.900	2.14E-01	Pearce and Kay (1987)
127	200	473	20.80	2.130	4.67E-01	Pearce and Kay (1987)
128	200	473	49.30	3.000	4.27E-01	Pearce and Kay (1987)
129	200	473	78.50	5.050	5.70E-01	Pearce and Kay (1987)
130	200	473	100.0	5.850	5.85E-01	Pearce and Kay (1987)
131	240	513	49.30	17.10	2.44E+00	Pearce and Kay (1987)
132	250	523	49.30	17.00	2.42E+00	Pearce and Kay (1987)
133	250	523	49.30	19.55	2.78E+00	Pearce and Kay (1987)
134	250	523	78.50	33.70	3.80E+00	Pearce and Kay (1987)
135	34.2	307.2	2.67	0.003092	1.89E-03	Ritchie (1984)
136	40	313	2.67	0.004168	2.55E-03	Ritchie (1984)

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obs.	TEMPERATURE		P of H2O	rate constant	k'	REFERENCE*
	(C)	(K)	(kPa)	k, mg/cm ² /hr	mg/cm ² /h/kPa ^{0.5}	
137	50	323	2.67	0.006050	3.71E-03	Ritchie (1984)
138	50	323	2.67	0.006722	4.12E-03	Ritchie (1984)
139	60	333	2.67	0.01035	6.34E-03	Ritchie (1984)
140	60	333	2.67	0.01048	6.42E-03	Ritchie (1984)
141	70	343	2.67	0.01384	8.48E-03	Ritchie (1984)
142	70	343	2.67	0.01653	1.01E-02	Ritchie (1984)
143	80	353	2.67	0.02057	1.26E-02	Ritchie (1984)
144	80	353	2.67	0.02084	1.28E-02	Ritchie (1984)
145	30	303	3.19	0.002957	1.66E-03	Ritchie (1986)
146	30.1	303.1	1.22	0.001344	1.22E-03	Ritchie (1986)
147	30.1	303.1	2.29	0.002420	1.60E-03	Ritchie (1986)
148	40	313	1.21	0.001478	1.34E-03	Ritchie (1986)
149	40	313	1.31	0.001747	1.53E-03	Ritchie (1986)
150	40	313	2.84	0.004168	2.47E-03	Ritchie (1986)
151	40	313	4.24	0.004168	2.02E-03	Ritchie (1986)
152	40	313	4.24	0.004302	2.09E-03	Ritchie (1986)
153	40	313	4.24	0.004571	2.22E-03	Ritchie (1986)
154	40	313	5.53	0.004974	2.11E-03	Ritchie (1986)
155	49.5	322.5	1.22	0.004436	4.01E-03	Ritchie (1986)
156	49.9	322.9	7.65	0.01157	4.18E-03	Ritchie (1986)
157	50	323	7.37	0.009976	3.67E-03	Ritchie (1986)
158	50	323	9.38	0.008739	2.85E-03	Ritchie (1986)
159	50.1	323.1	1.23	0.004705	4.25E-03	Ritchie (1986)
160	50.1	323.1	4.34	0.007892	3.79E-03	Ritchie (1986)
161	50.3	323.3	4.32	0.005539	2.67E-03	Ritchie (1986)
162	50.9	323.9	4.47	0.008013	3.79E-03	Ritchie (1986)
163	59.9	332.9	7.65	0.01327	4.80E-03	Ritchie (1986)
164	59.9	332.9	12.61	0.01747	4.92E-03	Ritchie (1986)
165	60	333	1.25	0.01025	9.15E-03	Ritchie (1986)
166	60	333	3.19	0.008591	4.81E-03	Ritchie (1986)
167	60	333	7.45	0.01052	3.85E-03	Ritchie (1986)
168	60	333	9.64	0.01492	4.81E-03	Ritchie (1986)
169	60	333	12.32	0.03307	9.42E-03	Ritchie (1986)
170	60.1	333.1	2.40	0.008564	5.53E-03	Ritchie (1986)
171	60.5	333.5	12.46	0.02756	7.81E-03	Ritchie (1986)
172	60.9	333.9	4.24	0.01101	5.35E-03	Ritchie (1986)
173	61.9	334.9	15.51	0.02151	5.46E-03	Ritchie (1986)
174	69.4	342.4	12.02	0.02500	7.21E-03	Ritchie (1986)
175	70	343	7.79	0.02420	8.67E-03	Ritchie (1986)
176	70	343	12.33	0.03321	9.46E-03	Ritchie (1986)
177	70.1	343.1	1.25	0.01250	1.12E-02	Ritchie (1986)
178	70.1	343.1	2.35	0.01747	1.14E-02	Ritchie (1986)
179	70.1	343.1	2.38	0.01667	1.08E-02	Ritchie (1986)
180	70.1	343.1	2.50	0.01492	9.43E-03	Ritchie (1986)
181	70.1	343.1	4.26	0.01640	7.95E-03	Ritchie (1986)
182	70.1	343.1	4.32	0.01936	9.32E-03	Ritchie (1986)

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obs.	TEMPERATURE		P of H2O	rate constant	k'	REFERENCE*
	(C)	(K)	(kPa)	k, mg/cm ² /hr	mg/cm ² /h/kPa ^{0.5}	
183	70.1	343.1	5.66	0.02084	8.76E-03	Ritchie (1986)
184	70.1	343.1	5.76	0.02218	9.24E-03	Ritchie (1986)
185	70.1	343.1	5.76	0.02904	1.21E-02	Ritchie (1986)
186	70.1	343.1	7.45	0.01855	6.80E-03	Ritchie (1986)
187	70.1	343.1	7.51	0.02635	9.62E-03	Ritchie (1986)
188	70.1	343.1	7.51	0.02769	1.01E-02	Ritchie (1986)
189	70.1	343.1	9.67	0.03052	9.82E-03	Ritchie (1986)
190	70.1	343.1	9.79	0.02635	8.42E-03	Ritchie (1986)
191	70.1	343.1	12.45	0.04705	1.33E-02	Ritchie (1986)
192	70.1	343.1	12.51	0.03724	1.05E-02	Ritchie (1986)
193	70.1	343.1	15.95	0.03321	8.32E-03	Ritchie (1986)
194	70.1	343.1	19.93	0.04705	1.05E-02	Ritchie (1986)
195	70.1	343.1	20.36	0.03885	8.61E-03	Ritchie (1986)
196	70.6	343.6	20.45	0.05539	1.22E-02	Ritchie (1986)
197	70.9	343.9	6.30	0.01747	6.96E-03	Ritchie (1986)
198	71.2	344.2	12.75	0.02877	8.06E-03	Ritchie (1986)
199	71.4	344.4	24.02	0.03751	7.65E-03	Ritchie (1986)
200	80.0	353	4.26	0.02393	1.16E-02	Ritchie (1986)
201	80.0	353	8.10	0.03764	1.32E-02	Ritchie (1986)
202	80.0	353	12.35	0.05122	1.46E-02	Ritchie (1986)
203	80.0	353	19.93	0.05660	1.27E-02	Ritchie (1986)
204	80.0	353	19.93	0.05902	1.32E-02	Ritchie (1986)
205	80.0	353	35.41	0.06991	1.17E-02	Ritchie (1986)
206	80.1	353.1	20.10	0.07206	1.61E-02	Ritchie (1986)
207	80.2	353.2	20.37	0.05136	1.14E-02	Ritchie (1986)
208	80.2	353.2	31.83	0.1025	1.82E-02	Ritchie (1986)
209	80.3	353.3	4.36	0.03240	1.55E-02	Ritchie (1986)
210	80.4	353.4	1.25	0.01667	1.49E-02	Ritchie (1986)
211	80.4	353.4	1.40	0.02110	1.79E-02	Ritchie (1986)
212	80.4	353.4	2.50	0.02218	1.40E-02	Ritchie (1986)
213	80.5	353.5	2.41	0.02635	1.70E-02	Ritchie (1986)
214	80.5	353.5	4.24	0.03267	1.59E-02	Ritchie (1986)
215	80.5	353.5	7.36	0.03737	1.38E-02	Ritchie (1986)
216	80.5	353.5	12.56	0.04853	1.37E-02	Ritchie (1986)
217	80.5	353.5	19.82	0.07368	1.65E-02	Ritchie (1986)
218	80.5	353.5	31.37	0.09694	1.73E-02	Ritchie (1986)
219	80.6	353.6	7.42	0.03939	1.45E-02	Ritchie (1986)
220	81.2	354.2	12.26	0.05042	1.44E-02	Ritchie (1986)
221	81.4	354.4	19.68	0.06547	1.48E-02	Ritchie (1986)
222	57	330	1.73	0.005915	4.50E-03	Waber (1958)
223	75	348	19.26	0.02016	4.59E-03	Waber (1958)
224	150	423	101.3	2.156	2.14E-01	Wathen (1943)
225	200	473	101.3	16.04	1.59E+00	Wathen (1943)
226	250	523	101.3	161.3	1.60E+01	Wathen (1943)
227	100	373	0.27	0.02200	4.27E-02	Weirick (1984)
228	100	373	0.27	0.02250	4.36E-02	Weirick (1984)

obs.	TEMPERATURE		P of H2O	rate constant	k'	REFERENCE*
	(C)	(K)	(kPa)	k, mg/cm ² /hr	mg/cm ² /h/kPa ^{0.5}	
229	100	373	0.27	0.02300	4.46E-02	Weirick (1984)
230	100	373	0.50	0.02900	4.10E-02	Weirick (1984)
231	100	373	0.67	0.03400	4.17E-02	Weirick (1984)
232	100	373	0.67	0.03500	4.29E-02	Weirick (1984)
233	100	373	0.67	0.04200	5.15E-02	Weirick (1984)
234	100	373	1.33	0.04800	4.16E-02	Weirick (1984)
235	100	373	1.33	0.05000	4.33E-02	Weirick (1984)
236	100	373	2.00	0.05600	3.96E-02	Weirick (1984)
237	100	373	2.00	0.05800	4.10E-02	Weirick (1984)
238	100	373	2.00	0.06100	4.31E-02	Weirick (1984)
239	100	373	2.67	0.06500	3.98E-02	Weirick (1984)
240	100	373	2.67	0.06700	4.10E-02	Weirick (1984)
241	100	373	3.00	0.08800	5.08E-02	Weirick (1984)

*References can be found in Abrefah and Sell (1999).

Table F-2.2. Spreadsheet Output of Statistical Calculations of Transformed Literature Review Data in Table F-2.1 (Page 1 of 6).

obs.	temp	1/T(K ⁻¹)	log k'				
	(C)	X	Y	X*Y	(X-aveX) ²	Yhat	(Y-Yhat) ²
1	65	2.959E-03	-1.7399	-5.148E-03	6.176E-08	-2.0785	1.146E-01
2	80	2.833E-03	-1.4703	-4.165E-03	1.508E-08	-1.7809	9.649E-02
3	100	2.681E-03	-1.4897	-3.994E-03	8.467E-10	-1.4214	4.671E-03
4	100	2.681E-03	-1.4766	-3.959E-03	8.467E-10	-1.4214	3.048E-03
5	100	2.681E-03	-1.5205	-4.076E-03	8.467E-10	-1.4214	9.832E-03
6	100	2.681E-03	-1.5363	-4.119E-03	8.467E-10	-1.4214	1.322E-02
7	100	2.681E-03	-1.5617	-4.187E-03	8.467E-10	-1.4214	1.970E-02
8	100	2.681E-03	-1.4079	-3.775E-03	8.467E-10	-1.4214	1.815E-04
9	100	2.681E-03	-1.4515	-3.891E-03	8.467E-10	-1.4214	9.068E-04
10	100	2.681E-03	-1.1973	-3.210E-03	8.467E-10	-1.4214	5.019E-02
11	80	2.833E-03	-1.7306	-4.903E-03	1.508E-08	-1.7809	2.525E-03
12	100	2.681E-03	-1.7632	-4.727E-03	8.467E-10	-1.4214	1.168E-01
13	62	2.985E-03	-2.0705	-6.181E-03	7.563E-08	-2.1412	4.991E-03
14	80	2.833E-03	-1.7975	-5.092E-03	1.508E-08	-1.7809	2.764E-04
15	100	2.681E-03	-1.1661	-3.126E-03	8.467E-10	-1.4214	6.517E-02
16	100	2.681E-03	-1.1945	-3.202E-03	8.467E-10	-1.4214	5.148E-02
17	100	2.681E-03	-1.5475	-4.149E-03	8.467E-10	-1.4214	1.590E-02
18	100	2.681E-03	-1.2614	-3.382E-03	8.467E-10	-1.4214	2.558E-02
19	100	2.681E-03	-1.3477	-3.613E-03	8.467E-10	-1.4214	5.430E-03
20	100	2.681E-03	-1.3091	-3.510E-03	8.467E-10	-1.4214	1.260E-02
21	100	2.681E-03	-1.2703	-3.406E-03	8.467E-10	-1.4214	2.282E-02
22	100	2.681E-03	-1.3186	-3.535E-03	8.467E-10	-1.4214	1.057E-02
23	100	2.681E-03	-1.2606	-3.380E-03	8.467E-10	-1.4214	2.585E-02
24	100	2.681E-03	-1.3392	-3.590E-03	8.467E-10	-1.4214	6.751E-03
25	100	2.681E-03	-1.2255	-3.285E-03	8.467E-10	-1.4214	3.838E-02
26	100	2.681E-03	-1.2097	-3.243E-03	8.467E-10	-1.4214	4.479E-02

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	temp	1/T(K ⁻¹)	log k'				
obs.	(C)	X	Y	X*Y	(X-aveX) ²	Yhat	(Y-Yhat) ²
27	100	2.681E-03	-1.2002	-3.218E-03	8.467E-10	-1.4214	4.892E-02
28	100	2.681E-03	-1.1817	-3.168E-03	8.467E-10	-1.4214	5.744E-02
29	25	3.356E-03	-2.8188	-9.459E-03	4.169E-07	-3.0184	3.983E-02
30	40	3.195E-03	-2.4898	-7.955E-03	2.351E-07	-2.6378	2.189E-02
31	40	3.195E-03	-2.5232	-8.061E-03	2.351E-07	-2.6378	1.312E-02
32	199	2.119E-03	-0.4676	-9.907E-04	3.498E-07	-0.0904	1.423E-01
33	199	2.119E-03	-0.3148	-6.670E-04	3.498E-07	-0.0904	5.034E-02
34	200	2.114E-03	-0.3065	-6.480E-04	3.551E-07	-0.0798	5.138E-02
35	201	2.110E-03	-0.5263	-1.110E-03	3.604E-07	-0.0693	2.089E-01
36	201	2.110E-03	-0.5150	-1.087E-03	3.604E-07	-0.0693	1.987E-01
37	201	2.110E-03	-0.4928	-1.040E-03	3.604E-07	-0.0693	1.794E-01
38	250	1.912E-03	0.3045	5.822E-04	6.368E-07	0.3986	8.851E-03
39	250	1.912E-03	0.3741	7.152E-04	6.368E-07	0.3986	6.005E-04
40	252	1.905E-03	0.0009	1.655E-06	6.485E-07	0.4158	1.722E-01
41	252	1.905E-03	0.0268	5.108E-05	6.485E-07	0.4158	1.513E-01
42	285	1.792E-03	0.5799	1.039E-03	8.426E-07	0.6824	1.051E-02
43	285	1.792E-03	0.6207	1.112E-03	8.426E-07	0.6824	3.812E-03
44	160	2.309E-03	-0.9230	-2.132E-03	1.605E-07	-0.5421	1.451E-01
45	200	2.114E-03	-0.3209	-6.785E-04	3.551E-07	-0.0798	5.812E-02
46	200	2.114E-03	-0.2240	-4.736E-04	3.551E-07	-0.0798	2.079E-02
47	200	2.114E-03	-0.2240	-4.736E-04	3.551E-07	-0.0798	2.079E-02
48	230	1.988E-03	0.2531	5.032E-04	5.213E-07	0.2186	1.190E-03
49	230	1.988E-03	0.2531	5.032E-04	5.213E-07	0.2186	1.190E-03
50	230	1.988E-03	0.9801	1.949E-03	5.213E-07	0.2186	5.799E-01
51	250	1.912E-03	0.7302	1.396E-03	6.368E-07	0.3986	1.100E-01
52	250	1.912E-03	0.9801	1.874E-03	6.368E-07	0.3986	3.382E-01
53	250	1.912E-03	0.9801	1.874E-03	6.368E-07	0.3986	3.382E-01
54	270	1.842E-03	1.0064	1.853E-03	7.542E-07	0.5652	1.947E-01
55	270	1.842E-03	1.0547	1.942E-03	7.542E-07	0.5652	2.396E-01
56	270	1.842E-03	1.0547	1.942E-03	7.542E-07	0.5652	2.396E-01
57	200	2.114E-03	0.1455	3.076E-04	3.551E-07	-0.0798	5.078E-02
58	250	1.912E-03	0.9000	1.721E-03	6.368E-07	0.3986	2.515E-01
59	100	2.681E-03	-0.8555	-2.294E-03	8.467E-10	-1.4214	3.202E-01
60	100	2.681E-03	-0.9037	-2.423E-03	8.467E-10	-1.4214	2.680E-01
61	150	2.364E-03	-0.9080	-2.146E-03	1.197E-07	-0.6713	5.600E-02
62	150	2.364E-03	-0.5890	-1.392E-03	1.197E-07	-0.6713	6.783E-03
63	150	2.364E-03	-0.6194	-1.464E-03	1.197E-07	-0.6713	2.692E-03
64	75	2.874E-03	-1.9673	-5.653E-03	2.673E-08	-1.8772	8.106E-03
65	75	2.874E-03	-2.1205	-6.093E-03	2.673E-08	-1.8772	5.916E-02
66	75	2.874E-03	-2.0436	-5.872E-03	2.673E-08	-1.8772	2.768E-02
67	75	2.874E-03	-1.9698	-5.660E-03	2.673E-08	-1.8772	8.573E-03
68	75	2.874E-03	-1.9279	-5.540E-03	2.673E-08	-1.8772	2.570E-03
69	80	2.833E-03	-1.2735	-3.608E-03	1.508E-08	-1.7809	2.575E-01
70	80	2.833E-03	-1.2324	-3.491E-03	1.508E-08	-1.7809	3.009E-01
71	80	2.833E-03	-1.2605	-3.571E-03	1.508E-08	-1.7809	2.708E-01

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	temp	1/T(K ⁻¹)	log k'				
obs.	(C)	X	Y	X*Y	(X-aveX) ²	Yhat	(Y-Yhat) ²
72	98	2.695E-03	-1.1151	-3.006E-03	2.145E-10	-1.4556	1.159E-01
73	60	3.003E-03	-2.2053	-6.623E-03	8.581E-08	-2.1836	4.718E-04
74	75	2.874E-03	-2.7345	-7.858E-03	2.673E-08	-1.8772	7.349E-01
75	35	3.247E-03	-2.4666	-8.009E-03	2.880E-07	-2.7605	8.636E-02
76	50	3.096E-03	-2.0951	-6.486E-03	1.489E-07	-2.4036	9.519E-02
77	65	2.959E-03	-1.7378	-5.141E-03	6.176E-08	-2.0785	1.161E-01
78	70	2.915E-03	-2.1262	-6.199E-03	4.218E-08	-1.9764	2.244E-02
79	70	2.915E-03	-2.0861	-6.082E-03	4.218E-08	-1.9764	1.204E-02
80	80	2.833E-03	-1.4678	-4.158E-03	1.508E-08	-1.7809	9.803E-02
81	100	2.681E-03	-1.1969	-3.209E-03	8.467E-10	-1.4214	5.037E-02
82	100	2.681E-03	-1.6284	-4.366E-03	8.467E-10	-1.4214	4.285E-02
83	100	2.681E-03	-1.2953	-3.473E-03	8.467E-10	-1.4214	1.589E-02
84	100	2.681E-03	-1.3543	-3.631E-03	8.467E-10	-1.4214	4.496E-03
85	100	2.681E-03	-1.4120	-3.786E-03	8.467E-10	-1.4214	8.739E-05
86	100	2.681E-03	-1.2581	-3.373E-03	8.467E-10	-1.4214	2.666E-02
87	100	2.681E-03	-1.3130	-3.520E-03	8.467E-10	-1.4214	1.175E-02
88	100	2.681E-03	-1.3813	-3.703E-03	8.467E-10	-1.4214	1.605E-03
89	100	2.681E-03	-1.5290	-4.099E-03	8.467E-10	-1.4214	1.159E-02
90	100	2.681E-03	-1.3887	-3.723E-03	8.467E-10	-1.4214	1.069E-03
91	100	2.681E-03	-1.3627	-3.653E-03	8.467E-10	-1.4214	3.444E-03
92	100	2.681E-03	-1.2522	-3.357E-03	8.467E-10	-1.4214	2.863E-02
93	100	2.681E-03	-1.3026	-3.492E-03	8.467E-10	-1.4214	1.412E-02
94	100	2.681E-03	-1.2879	-3.453E-03	8.467E-10	-1.4214	1.782E-02
95	100	2.681E-03	-1.2661	-3.394E-03	8.467E-10	-1.4214	2.410E-02
96	100	2.681E-03	-1.3478	-3.613E-03	8.467E-10	-1.4214	5.419E-03
97	100	2.681E-03	-1.2695	-3.403E-03	8.467E-10	-1.4214	2.307E-02
98	100	2.681E-03	-1.2367	-3.316E-03	8.467E-10	-1.4214	3.411E-02
99	100	2.681E-03	-1.2332	-3.306E-03	8.467E-10	-1.4214	3.539E-02
100	100	2.681E-03	-1.2509	-3.354E-03	8.467E-10	-1.4214	2.906E-02
101	100	2.681E-03	-1.1969	-3.209E-03	8.467E-10	-1.4214	5.037E-02
102	20	3.413E-03	-2.8056	-9.575E-03	4.941E-07	-3.1539	1.214E-01
103	22	3.390E-03	-2.8796	-9.761E-03	4.621E-07	-3.0992	4.823E-02
104	22	3.390E-03	-2.6066	-8.836E-03	4.621E-07	-3.0992	2.427E-01
105	40	3.195E-03	-2.6502	-8.467E-03	2.351E-07	-2.6378	1.540E-04
106	40	3.195E-03	-2.3491	-7.505E-03	2.351E-07	-2.6378	8.330E-02
107	50	3.096E-03	-2.4174	-7.484E-03	1.489E-07	-2.4036	1.900E-04
108	50	3.096E-03	-2.3762	-7.357E-03	1.489E-07	-2.4036	7.557E-04
109	60	3.003E-03	-2.2645	-6.800E-03	8.581E-08	-2.1836	6.548E-03
110	70	2.915E-03	-2.1264	-6.199E-03	4.218E-08	-1.9764	2.250E-02
111	70	2.915E-03	-2.1264	-6.199E-03	4.218E-08	-1.9764	2.250E-02
112	74	2.882E-03	-2.0746	-5.979E-03	2.951E-08	-1.8968	3.162E-02
113	74	2.882E-03	-2.0746	-5.979E-03	2.951E-08	-1.8968	3.162E-02
114	105	2.646E-03	-2.4829	-6.569E-03	4.168E-09	-1.3374	1.312E+00
115	105	2.646E-03	-1.5709	-4.156E-03	4.168E-09	-1.3374	5.448E-02
116	105	2.646E-03	-1.3979	-3.698E-03	4.168E-09	-1.3374	3.660E-03

	temp	1/T(K ⁻¹)	log k'				
obs.	(C)	X	Y	X*Y	(X-aveX) ²	Yhat	(Y-Yhat) ²
117	150	2.364E-03	-0.9066	-2.143E-03	1.197E-07	-0.6713	5.537E-02
118	150	2.364E-03	-1.0156	-2.401E-03	1.197E-07	-0.6713	1.185E-01
119	150	2.364E-03	-0.9515	-2.249E-03	1.197E-07	-0.6713	7.848E-02
120	150	2.364E-03	-0.9891	-2.338E-03	1.197E-07	-0.6713	1.010E-01
121	150	2.364E-03	-0.9714	-2.296E-03	1.197E-07	-0.6713	9.003E-02
122	150	2.364E-03	-0.9599	-2.269E-03	1.197E-07	-0.6713	8.330E-02
123	150	2.364E-03	-0.8471	-2.003E-03	1.197E-07	-0.6713	3.089E-02
124	180	2.208E-03	-0.5864	-1.294E-03	2.526E-07	-0.3008	8.156E-02
125	180	2.208E-03	-0.5746	-1.268E-03	2.526E-07	-0.3008	7.498E-02
126	180	2.208E-03	-0.6687	-1.476E-03	2.526E-07	-0.3008	1.354E-01
127	200	2.114E-03	-0.3307	-6.991E-04	3.551E-07	-0.0798	6.291E-02
128	200	2.114E-03	-0.3693	-7.808E-04	3.551E-07	-0.0798	8.379E-02
129	200	2.114E-03	-0.2441	-5.162E-04	3.551E-07	-0.0798	2.700E-02
130	200	2.114E-03	-0.2328	-4.923E-04	3.551E-07	-0.0798	2.341E-02
131	240	1.949E-03	0.3866	7.536E-04	5.787E-07	0.3103	5.812E-03
132	250	1.912E-03	0.3840	7.343E-04	6.368E-07	0.3986	2.111E-04
133	250	1.912E-03	0.4447	8.503E-04	6.368E-07	0.3986	2.131E-03
134	250	1.912E-03	0.5802	1.109E-03	6.368E-07	0.3986	3.299E-02
135	34.2	3.255E-03	-2.7227	-8.863E-03	2.972E-07	-2.7805	3.346E-03
136	40	3.195E-03	-2.5930	-8.284E-03	2.351E-07	-2.6378	2.004E-03
137	50	3.096E-03	-2.4312	-7.527E-03	1.489E-07	-2.4036	7.577E-04
138	50	3.096E-03	-2.3854	-7.385E-03	1.489E-07	-2.4036	3.319E-04
139	60	3.003E-03	-2.1980	-6.601E-03	8.581E-08	-2.1836	2.072E-04
140	60	3.003E-03	-2.1926	-6.584E-03	8.581E-08	-2.1836	8.051E-05
141	70	2.915E-03	-2.0718	-6.040E-03	4.218E-08	-1.9764	9.105E-03
142	70	2.915E-03	-1.9947	-5.815E-03	4.218E-08	-1.9764	3.343E-04
143	80	2.833E-03	-1.8997	-5.382E-03	1.508E-08	-1.7809	1.411E-02
144	80	2.833E-03	-1.8940	-5.366E-03	1.508E-08	-1.7809	1.280E-02
145	30	3.300E-03	-2.7807	-9.177E-03	3.484E-07	-2.8873	1.137E-02
146	30.1	3.299E-03	-2.9139	-9.614E-03	3.471E-07	-2.8848	8.489E-04
147	30.1	3.299E-03	-2.7957	-9.224E-03	3.471E-07	-2.8848	7.926E-03
148	40	3.195E-03	-2.8715	-9.174E-03	2.351E-07	-2.6378	5.465E-02
149	40	3.195E-03	-2.8167	-8.999E-03	2.351E-07	-2.6378	3.201E-02
150	40	3.195E-03	-2.6067	-8.328E-03	2.351E-07	-2.6378	9.677E-04
151	40	3.195E-03	-2.6938	-8.606E-03	2.351E-07	-2.6378	3.135E-03
152	40	3.195E-03	-2.6800	-8.562E-03	2.351E-07	-2.6378	1.785E-03
153	40	3.195E-03	-2.6537	-8.478E-03	2.351E-07	-2.6378	2.531E-04
154	40	3.195E-03	-2.6747	-8.545E-03	2.351E-07	-2.6378	1.364E-03
155	49.5	3.101E-03	-2.3967	-7.432E-03	1.527E-07	-2.4150	3.345E-04
156	49.9	3.097E-03	-2.3786	-7.366E-03	1.497E-07	-2.4059	7.472E-04
157	50	3.096E-03	-2.4349	-7.538E-03	1.489E-07	-2.4036	9.763E-04
158	50	3.096E-03	-2.5447	-7.878E-03	1.489E-07	-2.4036	1.990E-02
159	50.1	3.095E-03	-2.3719	-7.341E-03	1.482E-07	-2.4014	8.713E-04
160	50.1	3.095E-03	-2.4215	-7.495E-03	1.482E-07	-2.4014	4.051E-04
161	50.3	3.093E-03	-2.5742	-7.962E-03	1.467E-07	-2.3968	3.146E-02

	temp	1/T(K ⁻¹)	log k'				
obs.	(C)	X	Y	X*Y	(X-aveX) ²	Yhat	(Y-Yhat) ²
162	50.9	3.087E-03	-2.4211	-7.475E-03	1.424E-07	-2.3833	1.431E-03
163	59.9	3.004E-03	-2.3190	-6.966E-03	8.634E-08	-2.1857	1.777E-02
164	59.9	3.004E-03	-2.3081	-6.933E-03	8.634E-08	-2.1857	1.497E-02
165	60	3.003E-03	-2.0384	-6.121E-03	8.581E-08	-2.1836	2.107E-02
166	60	3.003E-03	-2.3176	-6.960E-03	8.581E-08	-2.1836	1.795E-02
167	60	3.003E-03	-2.4140	-7.249E-03	8.581E-08	-2.1836	5.309E-02
168	60	3.003E-03	-2.3182	-6.962E-03	8.581E-08	-2.1836	1.812E-02
169	60	3.003E-03	-2.0259	-6.084E-03	8.581E-08	-2.1836	2.488E-02
170	60.1	3.002E-03	-2.2573	-6.777E-03	8.529E-08	-2.1815	5.757E-03
171	60.5	2.999E-03	-2.1075	-6.319E-03	8.320E-08	-2.1729	4.285E-03
172	60.9	2.995E-03	-2.2720	-6.804E-03	8.114E-08	-2.1644	1.157E-02
173	61.9	2.986E-03	-2.2627	-6.756E-03	7.612E-08	-2.1433	1.425E-02
174	69.4	2.921E-03	-2.1420	-6.256E-03	4.431E-08	-1.9885	2.358E-02
175	70	2.915E-03	-2.0619	-6.011E-03	4.218E-08	-1.9764	7.314E-03
176	70	2.915E-03	-2.0242	-5.901E-03	4.218E-08	-1.9764	2.289E-03
177	70.1	2.915E-03	-1.9517	-5.688E-03	4.184E-08	-1.9744	5.128E-04
178	70.1	2.915E-03	-1.9429	-5.663E-03	4.184E-08	-1.9744	9.917E-04
179	70.1	2.915E-03	-1.9661	-5.730E-03	4.184E-08	-1.9744	6.862E-05
180	70.1	2.915E-03	-2.0255	-5.903E-03	4.184E-08	-1.9744	2.611E-03
181	70.1	2.915E-03	-2.0996	-6.120E-03	4.184E-08	-1.9744	1.569E-02
182	70.1	2.915E-03	-2.0307	-5.919E-03	4.184E-08	-1.9744	3.172E-03
183	70.1	2.915E-03	-2.0576	-5.997E-03	4.184E-08	-1.9744	6.933E-03
184	70.1	2.915E-03	-2.0341	-5.929E-03	4.184E-08	-1.9744	3.573E-03
185	70.1	2.915E-03	-1.9171	-5.588E-03	4.184E-08	-1.9744	3.279E-03
186	70.1	2.915E-03	-2.1676	-6.318E-03	4.184E-08	-1.9744	3.735E-02
187	70.1	2.915E-03	-2.0170	-5.879E-03	4.184E-08	-1.9744	1.819E-03
188	70.1	2.915E-03	-1.9955	-5.816E-03	4.184E-08	-1.9744	4.454E-04
189	70.1	2.915E-03	-2.0081	-5.853E-03	4.184E-08	-1.9744	1.137E-03
190	70.1	2.915E-03	-2.0747	-6.047E-03	4.184E-08	-1.9744	1.006E-02
191	70.1	2.915E-03	-1.8750	-5.465E-03	4.184E-08	-1.9744	9.868E-03
192	70.1	2.915E-03	-1.9776	-5.764E-03	4.184E-08	-1.9744	1.060E-05
193	70.1	2.915E-03	-2.0801	-6.063E-03	4.184E-08	-1.9744	1.118E-02
194	70.1	2.915E-03	-1.9772	-5.763E-03	4.184E-08	-1.9744	8.016E-06
195	70.1	2.915E-03	-2.0650	-6.019E-03	4.184E-08	-1.9744	8.215E-03
196	70.6	2.910E-03	-1.9119	-5.564E-03	4.012E-08	-1.9643	2.747E-03
197	70.9	2.908E-03	-2.1573	-6.273E-03	3.911E-08	-1.9583	3.961E-02
198	71.2	2.905E-03	-2.0938	-6.083E-03	3.811E-08	-1.9523	2.002E-02
199	71.4	2.904E-03	-2.1161	-6.144E-03	3.746E-08	-1.9483	2.816E-02
200	80	2.833E-03	-1.9358	-5.484E-03	1.508E-08	-1.7809	2.398E-02
201	80	2.833E-03	-1.8785	-5.321E-03	1.508E-08	-1.7809	9.519E-03
202	80	2.833E-03	-1.8364	-5.202E-03	1.508E-08	-1.7809	3.080E-03
203	80	2.833E-03	-1.8969	-5.374E-03	1.508E-08	-1.7809	1.347E-02
204	80	2.833E-03	-1.8788	-5.322E-03	1.508E-08	-1.7809	9.577E-03
205	80	2.833E-03	-1.9300	-5.467E-03	1.508E-08	-1.7809	2.224E-02
206	80.1	2.832E-03	-1.7939	-5.080E-03	1.488E-08	-1.7790	2.223E-04

	temp	1/T(K ⁻¹)	log k'				
obs.	(C)	X	Y	X*Y	(X-aveX) ²	Yhat	(Y-Yhat) ²
207	80.2	2.831E-03	-1.9439	-5.504E-03	1.469E-08	-1.7771	2.781E-02
208	80.2	2.831E-03	-1.7407	-4.928E-03	1.469E-08	-1.7771	1.325E-03
209	80.3	2.830E-03	-1.8092	-5.121E-03	1.449E-08	-1.7752	1.159E-03
210	80.4	2.830E-03	-1.8267	-5.169E-03	1.430E-08	-1.7733	2.850E-03
211	80.4	2.830E-03	-1.7480	-4.946E-03	1.430E-08	-1.7733	6.400E-04
212	80.4	2.830E-03	-1.8532	-5.244E-03	1.430E-08	-1.7733	6.381E-03
213	80.5	2.829E-03	-1.7705	-5.008E-03	1.411E-08	-1.7714	8.295E-07
214	80.5	2.829E-03	-1.7993	-5.090E-03	1.411E-08	-1.7714	7.767E-04
215	80.5	2.829E-03	-1.8610	-5.265E-03	1.411E-08	-1.7714	8.027E-03
216	80.5	2.829E-03	-1.8635	-5.272E-03	1.411E-08	-1.7714	8.478E-03
217	80.5	2.829E-03	-1.7812	-5.039E-03	1.411E-08	-1.7714	9.591E-05
218	80.5	2.829E-03	-1.7618	-4.984E-03	1.411E-08	-1.7714	9.321E-05
219	80.6	2.828E-03	-1.8398	-5.203E-03	1.392E-08	-1.7695	4.942E-03
220	81.2	2.823E-03	-1.8416	-5.199E-03	1.281E-08	-1.7582	6.967E-03
221	81.4	2.822E-03	-1.8310	-5.166E-03	1.246E-08	-1.7544	5.862E-03
222	57	3.030E-03	-2.3467	-7.111E-03	1.026E-07	-2.2482	9.698E-03
223	75	2.874E-03	-2.3378	-6.718E-03	2.673E-08	-1.8772	2.122E-01
224	150	2.364E-03	-0.6691	-1.582E-03	1.197E-07	-0.6713	4.755E-06
225	200	2.114E-03	0.2024	4.279E-04	3.551E-07	-0.0798	7.966E-02
226	250	1.912E-03	1.2048	2.304E-03	6.368E-07	0.3986	6.501E-01
227	100	2.681E-03	-1.3700	-3.673E-03	8.467E-10	-1.4214	2.637E-03
228	100	2.681E-03	-1.3603	-3.647E-03	8.467E-10	-1.4214	3.735E-03
229	100	2.681E-03	-1.3507	-3.621E-03	8.467E-10	-1.4214	4.993E-03
230	100	2.681E-03	-1.3871	-3.719E-03	8.467E-10	-1.4214	1.176E-03
231	100	2.681E-03	-1.3803	-3.700E-03	8.467E-10	-1.4214	1.691E-03
232	100	2.681E-03	-1.3677	-3.667E-03	8.467E-10	-1.4214	2.884E-03
233	100	2.681E-03	-1.2885	-3.454E-03	8.467E-10	-1.4214	1.766E-02
234	100	2.681E-03	-1.3812	-3.703E-03	8.467E-10	-1.4214	1.616E-03
235	100	2.681E-03	-1.3634	-3.655E-03	8.467E-10	-1.4214	3.356E-03
236	100	2.681E-03	-1.4022	-3.759E-03	8.467E-10	-1.4214	3.670E-04
237	100	2.681E-03	-1.3870	-3.718E-03	8.467E-10	-1.4214	1.183E-03
238	100	2.681E-03	-1.3651	-3.660E-03	8.467E-10	-1.4214	3.169E-03
239	100	2.681E-03	-1.4000	-3.753E-03	8.467E-10	-1.4214	4.562E-04
240	100	2.681E-03	-1.3869	-3.718E-03	8.467E-10	-1.4214	1.192E-03
241	100	2.681E-03	-1.2941	-3.469E-03	8.467E-10	-1.4214	1.620E-02
average of column>		2.7101E-03 =aveX	-1.49025 =aveY				
sum of column>>				-1.052= sumX*Y	3.320E-05 =SS _{xx}		1.291E+01 =SS _{resid}

input: T = temp(C) + 273; k' values from Table F-2.1;

$$Y_{\text{hat}} = 4.924118 - 2366.8686/T$$

Table F-2.3. Output from Excel Regression of the Literature Review Data.

Table F-2.5: Output from Excel Regression of the Literature Review Data.

SUMMARY OUTPUT	
Regression Statistics	
Multiple R	0.966997
R Square	0.935084
Adjusted R Square	0.934812
Standard Error	0.232441
Observations	241

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where $X=1/T(K^{-1})$ and $Y=\log k'$
as given in Table F-2.2.

ANOVA					
	df	SS	MS	F	Significance F
Regression	1	186.00332	186.0033	3442.683	6.3E-144
Residual	239	12.912834	0.054029		
Total	240	198.91616			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%
Intercept	4.924118	0.1103419	44.62598	6.6E-118	4.706751	5.141485
Slope	-2366.87	40.339048	-58.6744	6.3E-144	-2446.33	-2287.4

Result: $\log k' = 4.92411 - 2366.87*(1/T)$ with std error (se) = 0.2324

Table F-2.4. Spreadsheet Output for the Calculation of 95% Confidence Limits on the True Mean Value of the Regression of Literature Review Data.

Temp	X			Y (log k')			k', mg/cm ² -hr-kPa ^{0.5}		
(C)	1/T _n (K ⁻¹)	(X _n -aveX) ²	stdErrP	Y-hat	lower CL*	upper CL	lower CL	mean	upper CL
220	2.028E-03	4.647E-07	0.03131	0.1232	0.0615	0.1848	1.15E+00	1.33E+00	1.53E+00
200	2.114E-03	3.551E-07	0.02832	-0.0798	-0.1356	-0.0240	7.32E-01	8.32E-01	9.46E-01
180	2.208E-03	2.526E-07	0.02520	-0.3008	-0.3504	-0.2511	4.46E-01	5.00E-01	5.61E-01
160	2.309E-03	1.605E-07	0.02203	-0.5421	-0.5855	-0.4987	2.60E-01	2.87E-01	3.17E-01
140	2.421E-03	8.338E-08	0.01897	-0.8068	-0.8442	-0.7694	1.43E-01	1.56E-01	1.70E-01
120	2.545E-03	2.740E-08	0.01639	-1.0984	-1.1307	-1.0662	7.40E-02	7.97E-02	8.59E-02
100	2.681E-03	8.467E-10	0.01502	-1.4214	-1.4510	-1.3918	3.54E-02	3.79E-02	4.06E-02
80	2.833E-03	1.508E-08	0.01577	-1.7809	-1.8120	-1.7498	1.54E-02	1.66E-02	1.78E-02
60	3.003E-03	8.581E-08	0.01907	-2.1836	-2.2212	-2.1460	6.01E-03	6.55E-03	7.14E-03
40	3.195E-03	2.351E-07	0.02463	-2.6378	-2.6863	-2.5892	2.06E-03	2.30E-03	2.57E-03
20	3.413E-03	4.941E-07	0.03207	-3.1539	-3.2171	-3.0908	6.07E-04	7.02E-04	8.11E-04

Input: $Y_{hat} = 4.924118 - 2366.8686/T$,
 $n = 241$,
 $t(0.05, 239) = 1.9699$,
 $aveX = 2.7101E-3$,
 $se = 0.2324$,
 $SS_{xx} = 3.320E-05$.

Figure F-1. Confidence Limits on the Mean of Reaction Rate Data.

ANALYTICAL CALCULATIONS

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 Subject Hand Calculation Check of Calculations in Appendix F, HNF 4206
 Originator DJ Trimble Date 8-10-00
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Checks performed using HP425 calculator.

A. Checking Table F-1.2 in Appendix F of HNF 4206, Rev 1.
For obs. #4

$$X = \frac{1}{T} = (105 + 273)^{-1} = 378^{-1} = 2.6455E-3$$

$$k' = \frac{0.0243}{\sqrt{7.3}} = \frac{0.0243}{2.7018} = 8.9938E-3$$

$$Y = \log k' = \log 8.9938E-3 = -2.04606$$

$$XY = (2.6455E-3)(-2.04606) = -5.4128E-3$$

$$\bar{X} = \frac{\sum X}{n} = \frac{2.13249E-2}{9} = 2.3694E-3$$

$$(X - \bar{X})^2 = (378^{-1} - 2.3694E-3)^2 = (2.7606E-4)^2 \\ = 7.6214E-8$$

$$Y_{\text{hat}} = \hat{Y} = 5.665 - 2902./378 \\ = 5.665 - 7.6773 = -2.01225$$

$$(Y - \hat{Y})^2 = [-2.04606 - (-2.0134)]^2 \\ = (-3.3811E-2)^2 \\ = 1.1432E-3$$

$$\sum XY = 371^{-1}(-2.3098) + \dots + 402^{-1}(-1.3484) \\ = -2.7014E-2$$

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ANALYTICAL CALCULATIONS

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 Subject Hand Check of Calculations - Appendix F
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B. Check Table F-1.3

slope of regression line: $a = S_{xy} / S_{xx}$

$$\text{where } S_{xy} = \sum X_i Y_i - n \bar{Y} \bar{X}$$

$$= -2.701E-2 - 9(-1.2121)(0.0023694)$$

$$= -2.701E-2 + 2.5847$$

$$= -1.167E-3$$

$$S_{xx} = \sum (X_i - \bar{X})^2 = 4.0172E-7 \quad (\text{from Table F-1.2})$$

$$a = \frac{-1.167E-3}{4.0172E-7} = -2905.8$$

$$b = \bar{Y} - a \bar{X} = -1.2121 - (-2905.8)(0.0023694) \\ = -1.212 + 6.8846 = 5.672$$

$$SE(\text{std error}) = \left(\frac{SS_{\text{resid}}}{n-2} \right)^{\frac{1}{2}} = \left[\frac{\sum (Y_i - \hat{Y})^2}{n-2} \right]^{\frac{1}{2}} \\ = \left(\frac{0.48429}{9-2} \right)^{\frac{1}{2}} = (6.9184E-2)^{\frac{1}{2}} \\ = 0.26303 \quad \sum (Y_i - \hat{Y})^2 - \text{from Table F1.2}$$

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C. Checking Table F-1.4 at 160°C

$$(X_0 - \bar{X})^2 = \left(\frac{1}{160+273} - 0.0023694 \right)^2$$

$$= (-5.993\text{E-}5)^2 = 3.591\text{E-}9 \checkmark$$

$$\text{Std Err P} = \text{se} \left[\frac{1}{n} + \frac{(X_0 - \bar{X})^2}{S_{xx}} \right]^{\frac{1}{2}}$$

$$S_{xx} = 4.0172\text{E-}7 \text{ from Table F-1.2}$$

$$n = 9$$

$$\text{std Err P} = 0.2630 \left(\frac{1}{9} + \frac{3.591\text{E-}9}{4.0172\text{E-}7} \right)^{\frac{1}{2}}$$

$$= 0.2630 (0.12005)^{\frac{1}{2}}$$

$$= 0.091125 \checkmark$$

$$\hat{y} = 5.665 - \frac{2902}{160+273} = 5.665 - 6.702$$

$$= -1.03708 \checkmark$$

$$\text{upper CL} = \hat{y} + t \cdot \text{std Err P}$$

$$= -1.03708 + 2.3646(0.091125)$$

$$= 0.8216 \checkmark$$

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ANALYTICAL CALCULATIONS

Subject Hand Check of Calculations - Appendix F Page 4 of 6
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D. Check Table F-2.2 at obs. 238

$$X = \frac{1}{T} = (100 + 273)^{-1} = 2.68097 \text{E-}3 \checkmark$$

$$Y = \log k' = \log \left(\frac{0.06106}{\sqrt{2}} \right) = \log 4.313 \text{E-}2 \\ = -1.36519 \checkmark$$

$$XY = \left(\frac{1}{373} \right) (-1.36519) = -3.660 \text{E-}3 \checkmark$$

$$(X - \bar{X})^2 = \left(\frac{1}{373} - 2.7101 \text{E-}3 \right)^2 = 8.4884 \text{E-}10 \checkmark$$

$$\hat{Y} = 4.924118 - 2366.8686/373 \\ = -1.42137 \checkmark$$

~~$\hat{Y} - Y = -1.42137$~~ D J T 8-10-00

$$(Y - \hat{Y})^2 = [-1.36519 - (-1.42137)]^2 \\ = (0.0561892)^2 \\ = 3.1567 \checkmark$$

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ANALYTICAL CALCULATIONS

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E. Check Table F-2.3

slope of regression line: $a = S_{xy} / S_{xx}$ where $S_{xy} = \sum X_i Y_i - n \bar{X} \bar{Y}$

$$= -1.052 - 241(2.7101E-3)(-1.49024)$$

$$= -1.052 + \cancel{0.74423} 0.91333 \text{ DNT}$$

$$= \cancel{-0.30727} -7.86734E-2 \text{ DNT F-10-00}$$

$$S_{xx} = \sum (X - \bar{X})^2 = 3.320E-5 \text{ (Table F-2.2)}$$

$$a = \frac{\cancel{-0.30727} -7.86734E-2 \text{ DNT F-10-00}}{3.320E-5} = -2370 \checkmark$$

$$b(\text{intercept}) = \bar{Y} - a \bar{X}$$

$$= -1.49025 - (-2370)(2.7101E-3)$$

$$= -1.49025 + 6.42207 = 4.932 \checkmark$$

$$se = \left(\frac{SS_{\text{resid}}}{n-2} \right)^{\frac{1}{2}} = \left(\frac{\sum (Y_i - \hat{Y})^2}{n-2} \right)^{\frac{1}{2}}$$

$$= \left(\frac{12.91}{241-2} \right)^{\frac{1}{2}} = (0.054017)^{\frac{1}{2}}$$

$$= 0.2324 \checkmark$$

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ANALYTICAL CALCULATIONS

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Subject Hand Calculation Check - Appendix F HNF4206, Rev 1
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F. Checking Table F-2.4 at Temp = 80°C

$$X = \frac{1}{T_0} = \left(80 + 273\right)^{-1} = 353^{-1} = 2.83286 \text{E-}3 \quad \checkmark$$

~~DN 8-11-00~~

$$\hat{Y} = \frac{4.924118 - 2366.869}{80 + 273} = 4.924118 - 6.70501$$

$$= -1.78089 \quad \checkmark$$

$$(X_0 - \bar{X})^2 = \left(\frac{1}{353} - 2.7101 \text{E-}3\right)^2 = \frac{1.77806 \times 10^{-2}}{(1.22761 \text{E-}4)^2} \quad \checkmark$$

~~DN 8-11-00~~

$$= 1.50703 \text{E-}8 \quad \checkmark$$

$$\text{stdErrP} = \text{se} \left(\frac{1}{n} + \frac{(X_0 - \bar{X})^2}{SS_{XX}} \right)^{\frac{1}{2}}$$

$$= 0.2324 \left(\frac{1}{241} + \frac{1.507 \text{E-}8}{3.320 \text{E-}5} \right)^{\frac{1}{2}}$$

$$= 0.2324 (4.6033)^{\frac{1}{2}} = 1.0698 \text{E-}3 \quad \checkmark$$

~~DN 8-11-00~~

$$= 0.2324 \sqrt{4.6033 \text{E-}3} = 0.015768 \quad \checkmark$$

$$\text{lower CL} = \hat{Y} - t \cdot \text{stdErrP}$$

$$= -1.78089 - 1.9699 (0.015768)$$

$$= -1.812 \quad \checkmark$$

$$k' @ \text{lower CL} = 10^{-1.812}$$

$$= 1.542 \text{E-}2 \quad \checkmark$$

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 8-11-00

REVIEW CHECKLIST**Document Reviewed:**

HNF-4206, REV 1, APPENDIX F, SUPPORTING CALCULATIONS FOR REGRESSION ANALYSIS OF REACTION RATE DATA (OCRWM).

Scope of Review:

Equations used in the check of linear regression analyses by a spreadsheet function, and the calculations of confidence limits on the true mean value from the regressions of the data.

Yes No NA

☒	☐	☐	* Previous reviews complete and cover analysis, up to scope of this review, with no gaps.
☒	☐	☐	Problem completely defined.
☐	☐	☒	Accident scenarios developed in a clear and logical manner.
☒	☐	☐	Necessary assumptions explicitly stated and supported.
☐	☐	☒	Computer codes and data files documented.
☒	☐	☐	Data used in calculations explicitly stated in document.
☒	☐	☐	Data checked for consistency with original source information as applicable.
☐	☐	☒	Mathematical derivation checked including dimensional consistency of results.
☐	☐	☒	Models appropriate and used within range of validity or use outside range of established validity justified.
☒	☐	☐	Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations.
☐	☐	☒	Software input correct and consistent with document reviewed.
☐	☐	☒	Software output consistent with input and with results reported in document reviewed.
☒	☐	☐	Limits/criteria/guidelines applied to analysis results are appropriate and referenced. Limits/criteria/guidelines checked against references.
☐	☐	☒	Safety margins consistent with good engineering practices.
☒	☐	☐	Conclusions consistent with analytical results and applicable limits.
☒	☐	☐	Results and conclusions address all points required in the problem statement.
☐	☐	☒	Format consistent with appropriate NRC Regulatory Guide or other standards.
☐	☐	☒	* Review calculations, comments, and/or notes are attached.
☒	☐	☐	Document approved.

MICHAEL J PACKER

Reviewer (Printed Name and Signature)

8/9/00

Date

*Any calculations, comments, or notes generated as part of this review should be signed, dated and attached to this checklist. Such material should be labeled and recorded in such a manner as to be intelligible to a technically qualified third party.

CALCULATION DOCUMENT CHECKLIST

Calculation Title HNF-4206, REV 1, APPENDIX F, SUPPORTING CALCULATIONS FOR REGRESSION ANALYSIS OF REACTION RATE DATA (OCRWM)

Assignment Number

None

Identification Number

None

NOTE: This checklist applies only to documentation and does not include review of the accuracy or completeness of the calculations included within the documentation.

YES/NO/NA

- Yes 1. Is the correct calculation title used? *(title is for appendix, not original calculation)*
- Yes 2. Has this calculation been identified to a project, subproject, item of equipment, system, or system analysis?
- Yes 2a. If yes, is it identified in the title or document identification number? *(in original calculation title)*
- Yes 3. Has the person(s) names performing the calculation been included?
- Yes 4. Has the person(s) performing the calculation signed the calculation?
- Yes 5. Has the date of calculation submittal been included?
- Yes 6. Are the pages sequentially numbered?
- Yes 7. Has the calculation followed the format from the SNF Project Administrative Procedure 6-010 requirements?
- Yes 8. Has the proper information pertaining to computer usage been included?
- No 9. Has any part of this calculation been procured from contractors/subcontractors?
- N/A 9a. Has the procured calculation documentation been reviewed against documentation requirements in the procurement document(s)?
- Yes 10. Was an in-house review performed?
- Yes 10a. If yes, has the in-house reviewer(s) name been included?
- Yes 10b. If yes, has the in-house reviewer(s) signature been included?
- N/A 10c. If in-house review produced comment(s), has the comment(s) been dispositioned, action completed, and documented?
- Yes 10d. Is the review criteria used for the in-house review included?
- Yes 11. Will this calculation require an ECN to an existing calculation?
- No 12. Will the results from this calculation affect other related calculations?

Prepared By

DRH/uncan 8/22/00

Signature